

***Herstellung und Untersuchung
protonenleitender porös - aromatischer
Gerüstverbindungen***

Dissertation

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„Wer aufgehört hat, besser zu werden, der hat aufgehört gut zu sein“

(Philip Rosenthal)

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Abkürzungsverzeichnis

Abkürzung	Bedeutung
A	Fläche der Probe
Abb.	Abbildung
B ₀	Externes Magnetfeld
b _{1/2}	Halbwertsbreite/FWHM
BET	Brunauer, Emmet, Teller
BPP	Bloembergen, Purcell und Pound
C	Kondensator
COF	<i>covalent organic framework</i>
CIMPAF	Chloromethylen-PAF
CPE	<i>Constant Phase Element</i>
CTF	<i>covalent triazine framework</i>
ΔE	Energiedifferenz
D	Eigendiffusion
DSC	<i>differential scanning calorimetry</i>
E _A	Aktivierungsenergie
EDX	<i>energy dispersive X-ray</i>
EIS	Elektrochemische Impedanzspektroskopie
φ	Phasenverschiebung
FID	<i>free induction decay</i>
FWHM	<i>full width at half maximum</i>
γ	gyromagnetisches Verhältnis
GO	Graphenoxid
I	Stromstärke
I	Kernspin
I ₀	maximale Stromstärke
IEC	ion exchange capacity
Im	Imaginärteil
J	spektrale Dichte
k _B	Boltzmann-Konstante
L	Induktor
l	Dicke der Probe
μ	magnetisches Moment
M	makroskopische Magnetisierung
M ₀	maximale makroskopische Magnetisierung
M ₊ (t)	Abfall der Magnetisierung im FID
MOF	<i>metal organic framework</i>
N _α	Anzahl der Spins antiparallel zum externen Magnetfeld
N _β	Anzahl der Spins parallel zum externen Magnetfeld
NMR	<i>nuclear magnetic resonance</i>
ω	Frequenz
ω ₀	Resonanzfrequenz
PAF	<i>porous aromatic framework</i>
PBI	Polybenzimidazol
PEM	Polymer-Elektrolyt-Membran
POP	poröses organisches Polymere

Abkürzungsverzeichnis

PTFE	Polytetrafluorethylen
R	Widerstand
R	universelle Gaskonstante
r	Abstand
ρ	spez. Widerstand
Re	Realteil
RH	<i>relative humidity</i>
σ	spez. Leitfähigkeit
SEM	<i>scanning electron microscopy</i>
SFG	<i>static-field gradient</i>
SMPAF	Sulfonsäuremethylen-PAF
sPEEK	sulfoniertes Polyetheretherketon
sPSU	sulfoniertes Polysulfon
t	Zeit
T	Temperatur
T_1	Spin-Gitter-Relaxation, longitudinale Relaxation
T_2	Spin-Spin-Relaxation, transversale Relaxation
τ_c	Korrelationszeit
U	Spannung
U_0	maximale Spannung
XPS	<i>X-ray photoelectron spectroscopy</i>
Z	Impedanz
Z_0	maximale Impedanz

Zusammenfassung

Diese Arbeit beschäftigt sich mit der porösen, aromatischen Gerüstverbindung PAF-303 und ihren Derivaten in Bezug auf deren Protonenleitung und der Entwicklung einer Methode zur Untersuchung der zugrundeliegenden Mechanismen. Bei PAF-303 handelt es sich um eine amorphe Gerüstverbindung, die in ihrer Nahordnung durch eine adamantanartige Struktur abgebildet werden kann. Die Struktur wird durch drei linear verknüpfte Phenylringe, die durch sp^3 -hybridisierte Kohlenstoffatome verknüpft sind, aufgebaut. Diese Phenylringe in Verbindung mit der hochporösen und offenporigen Struktur der Gerüstverbindung ermöglichen eine postsynthetische Modifikation. So war es möglich, die nanoporöse Gerüstverbindung SPAF-303 mit drei Sulfonierungsgraden von 30 %, 50 % und 80 % herzustellen. Dabei verringerte sich die innere Oberfläche sowie das Porenvolumen drastisch. Durch Adsorption von Wasser war es möglich das Porenvolumen der Gerüstverbindung praktisch wieder vollständig zu regenerieren. Zudem zeigte das adsorbierte Wasser im Gegensatz zu dem *state of the art* Material Nafion® keinerlei Phasenseparation zwischen dem Wasser und der Gerüstverbindung, was unter anderem auf den starken Wechselwirkungen zwischen den hydrophilen Gruppen der Gerüstverbindung und den Wasser-Molekülen beruht. In Verbindung mit einer limitierten Beweglichkeit der Wasser-Moleküle bildet das System ein starkes Confinement.

Dieses starke Confinement besitzt eine Leitfähigkeit von bis zu 1 S cm^{-1} für die Gerüstverbindung SPAF-303_{0,5} bei 353 K und 100 % relativer Luftfeuchtigkeit. Die sehr gute Protonenleitfähigkeit konnte auf folgende Faktoren zurückgeführt werden. Die Sulfonsäuregruppen der Gerüstverbindungen führen zur Ausbildung zweier Wasser-Regime im Porensystem. Zum einen liegt Wasser in sehr starken Wechselwirkungen mit den Sulfonsäuregruppen vor, als sogenanntes immobilisiertes Wasser. Zum anderen ist Wasser im Innenraum der Pore vorhanden, das mobil ist. Ein Austausch zwischen diesen beiden Ensembles findet bei allen Sulfonierungsgraden und Luftfeuchtigkeiten statt. Die Diffusion des adsorbierten Wassers ist hierbei nahezu in der Größenordnung von reinem Wasser. Der Zusammenhang zwischen der mikro- und makroskopischen Leitfähigkeit sowie den Mechanismus konnte durch die Kombination von Methoden der Kernspinresonanz- und Impedanzspektroskopie herausgearbeitet werden. So konnte die Abhängigkeit der makroskopischen Leitfähigkeit von der mikroskopischen Diffusion und dem Austausch zwischen den beiden Wasser-Regimen aufgeklärt werden. Es hat sich hierbei herausgestellt, dass in diesem porösen System die Nanostrukturierung der Pore, alternierende Anordnung von

Zusammenfassung

hydrophilen und hydrophoben Gruppen mit der Konnektivität der Poren zueinander in Abhängigkeit des Wassergehalts in den Poren, den entscheidendsten Einfluss auf die Aktivierungsenergie und Leitfähigkeit des Systems hat, wohingegen die Ladungsträgerzahl eine untergeordnete Rolle einnehmen. So zeigte die Gerüstverbindung SPAF-303_{0,5} stets die niedrigste Aktivierungsenergie.

Eine Weiterentwicklung, basierend auf den gewonnenen Erkenntnissen, bildet das Netzwerk SMPAF-303. Dieses Netzwerk wurde ausgehend von PAF-303 über eine zweistufige postsynthetische Modifizierung hergestellt. Im ersten Schritt wurde an die Phenylringe eine Chloromethylen-Seitenkette addiert. Darauf folgte der Austausch der funktionellen Gruppe gegen Sulfonsäure. So war es möglich, die thermodynamisch stabile Sulfonsäuregruppe in das nanoporöse Netzwerk einzubringen. Neben der Aufklärung der Struktur und der erfolgreichen Synthese konnte gezeigt werden, dass die Seitengruppe stabil gegenüber aziden Bedingungen in Verbindung mit hohen Temperaturen ist, bei denen die Hydrolyse der Aryl-Sulfonsäuregruppe stattfindet. Es war möglich bei dem Netzwerk eine Seitenkette pro Wiederholungseinheit zu addieren, was einen Sulfonierungsgrad von 17 % widerspiegelt mit einer Leitfähigkeit von ca. $0,1 \text{ S cm}^{-1}$.

Die Ergebnisse aus der Untersuchung von SPAF-303 und SMPAF-303 ermöglichen weitere Strategien für die Darstellung neuer nanoporöser Gerüstverbindungen mit Seitenketten, die Proton-Donatoren beinhalten. Ziel wird es hierbei sein, die Nanostrukturierung des Porenraums zu vollziehen, sodass eine alternierende Polarität für die Absenkung der Aktivierungsenergie für die Protonenleitung vorliegt. Hierfür muss eine kontrollierte Alkylierung der Gerüstverbindung vollzogen werden, d.h. dass 50 % der Phenylringe postsynthetisch alkyliert werden müssten und anschließend zur Alkylsulfonsäure-Seitengruppe umgesetzt werden. Hierbei gilt es die Reaktion in einem geeigneten Lösungsmittel durchzuführen, sodass der Porenraum der Gerüstverbindung zugänglich ist und keine sterische Hinderung der Reaktionen vorliegt. Einen zweiten Ansatz bildet die Möglichkeit das Netzwerk aus Monomeren darzustellen, die bereits eine Seitengruppe beinhalten. Bei der Synthese der Gerüstverbindung wird sich aufgrund der sterischen Effekte der Linker-Moleküle mit dem Katalysator die Struktur der Gerüstverbindung selbst organisieren, wobei auszugehen ist, dass eine große Fehlordnung der adamantanartigen Struktur vorliegen wird. Es muss zudem eine mögliche Konkurrenzreaktion der Seitenkette sowie eine Passivierung des Katalysators durch die funktionelle Gruppe der Seitenkette ausgeschlossen werden. Das dadurch ausgebildete Confinement, basierend auf den starken Wechselwirkungen des Netzwerks mit den

Gastmolekülen, kann mittels der Kombination aus Impedanz- und NMR-Spektroskopie untersucht werden und der Leitungsmechanismus detailliert aufgeklärt werden.

Summary

This study focuses on the porous aromatic framework PAF-303 and its derivatives regarding their proton conductivity, as well as on the development of a methodology to investigate the underlying transport mechanisms. PAF-303 is an amorphous framework material whose short-range order can be described by an adamantane-like structure. The structure is built of three phenyl rings interconnected via sp^3 -hybridized carbon atoms. The combination of these phenyl rings with the highly porous and open-pore architecture of the framework enables post-synthetic modification. Based on this approach, the nanoporous framework SPAF-303 was obtained with three degrees of sulfonation degrees of about 30%, 50%, and 80%. With Increasing sulfonation degrees, the surface area and pore volume drastically reduce. However, upon water adsorption, the pore volume could be almost fully restored. In contrast to the state-of-the-art material Nafion[®], the adsorbed water in SPAF-303 exhibited no phase separation between the water and the framework. This behavior is attributed to strong interactions between the hydrophilic functional groups of the framework and water molecules. In combination with the restricted mobility of the confined water molecules, this results in a strong confinement regime.

This strong confinement yields proton conductivities of up to 1 S cm^{-1} for SPAF-303_{0.5} at 353 K and 100 % relative humidity. The exceptionally high proton conductivity can be attributed to several factors. The sulfonic acid groups within the framework give rise to two distinct water regimes in the pore system: the immobile water that is strongly bound to the sulfonic acid groups, and mobile water which is located inside the pore. Exchange between these two ensembles occurs for all sulfonation degrees and humidity conditions. The diffusion of adsorbed water was found to be nearly comparable to that of bulk water. By combining paramagnetic nuclear magnetic resonance (NMR) spectroscopy and impedance spectroscopy, the relationship between microscopic diffusion, exchange dynamics, and macroscopic conductivity was clarified. The results revealed that, in this porous system, the nano structuring of the pore is characterized by alternating arrangements of hydrophilic and hydrophobic groups, in combination with pore connectivity and its dependence on water content, are the dominant influence on activation energy and conductivity. The number of charge carriers plays only a secondary role. Notably, SPAF-303_{0.5} consistently exhibited the lowest activation energy.

Further development, based on these insights, is represented by the SMPAF-303 network. This material was synthesized from PAF-303 via a two-step post-synthetic modification. In the first step, a chloromethylene side chain was introduced onto the phenyl rings. In the second step, the functional group was replaced with a sulfonic acid group. This strategy allowed the

incorporation of the thermodynamically stable sulfonic acid group into the nanoporous framework. Structural characterization confirmed the successful synthesis and demonstrated that the side chain is stable under acidic conditions and elevated temperatures at which hydrolysis of aryl-sulfonic acid groups typically occurs. A degree of sulfonation of 17% which corresponds to one side chain per repeating unit, was achieved, resulting in a proton conductivity of approximately 0.1 S cm^{-1} .

The findings from SPAF-303 and SMPAF-303 provide a foundation for further strategies to design novel nanoporous frameworks with side chains containing proton-donating groups. The aim is to tailor the pore nanostructure to achieve alternating polarity, thereby lowering the activation energy for proton transport. One approach would be controlled alkylation of the framework, whereby 50% of the phenyl rings are post-synthetically alkylated and subsequently converted into alkyl-sulfonic acid side chains. This reaction must be conducted in a solvent that ensures pore accessibility and prevents steric hindrance during modification. A second approach involves synthesizing the framework directly from monomers that already contain side chains. In this case, due to steric effects between linker molecules and the catalyst, the framework structure is expected to self-organize, likely leading to a high degree of disorder within the adamantane-like network. Additionally, competitive side reactions involving the side chain, as well as catalyst passivation by the side-chain functional group, must be avoided. The resulting confinement, arising from strong interactions between the network and guest molecules, can be investigated using a combination of impedance spectroscopy and NMR spectroscopy, enabling a detailed elucidation of the conduction mechanism.

1. Einleitung

Die Energiewende erfordert ein Umdenken in der aktuellen Energiepolitik. Ziel ist es, nachhaltige und umweltfreundliche Energieträger zu nutzen.^[1] Wasserstoff hat sich in diesem Transformationsprozess als ein vielversprechender Bestandteil herausgestellt.^[2,3] So ist es möglich, diesen aus Überschüssen an elektrischer Energie nachhaltig aus Wasser zu generieren, zu speichern und anschließend bei Bedarf die in ihm gespeicherte chemische Energie wieder in elektrische Energie umzuwandeln.^[3] Die Reaktion von Wasser in Wasserstoff und Sauerstoff sowie die Rückreaktion erfolgt unter anderem in einem PEM-Elektrolyseur bzw. einer PEM-Brennstoffzelle.^[4,5]

Als zentrales Element der beiden Energiekonverter dient die Polymerelektrolytmembran (PEM) (Abb. 1).^[4-6] In dieser werden die erzeugten Protonen zwischen den beiden Elektroden transportiert. Neben dem Transport der Protonen muss die Membran die beiden Elektroden voneinander separieren, d. h. das verwendete Material muss elektrisch isolierend sein.^[7] Des Weiteren sind geforderte Eigenschaften der Membran Gasdichtheit, sodass eine Knallgasreaktion unterbunden wird, sowie eine hinreichende mechanische Stabilität aufweisen.^[7]

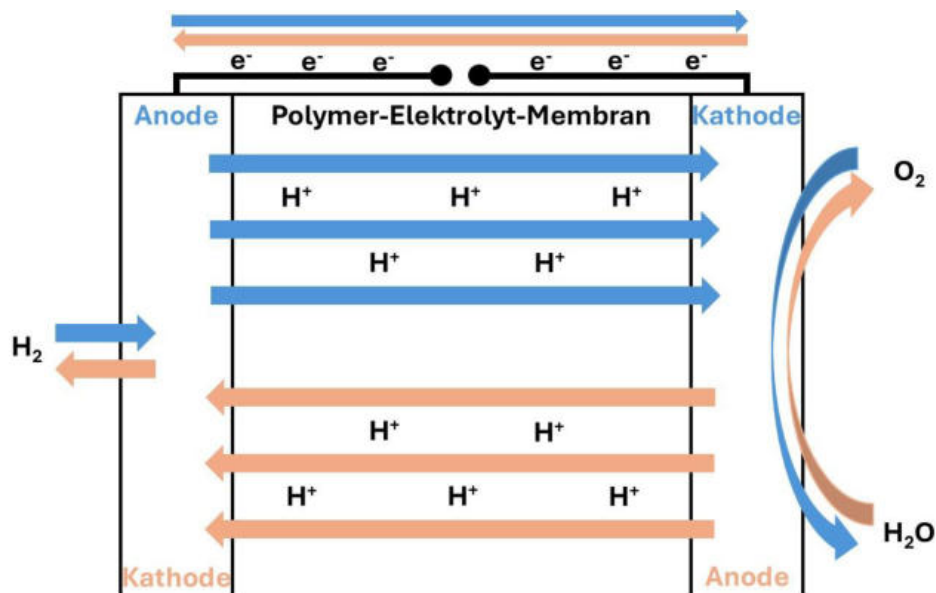


Abb. 1: Schematischer Aufbau der PEM-Brennstoffzelle (blau) und des PEM-Elektrolyseurs (rot).

Als *state of the art* Material wird zum jetzigen Zeitpunkt Nafion[®] verwendet.^[8] Das perfluorierte Ppropfcopolymer besitzt ein PTFE-Rückgrat, an das sulfonierte PTFE-

Einleitung

Seitenketten gepfropft sind.^[9] Das Rückgrat von Nafion[®] ist hydrophob und die Seitenketten bilden den hydrophilen Part des Polymers. Dies bewirkt eine Phasenseparation des Netzwerkes, sodass Kanäle gebildet werden, in denen Wasser eingelagert werden kann und die Protonenleitung dort stattfindet. Diese Struktur wird als Nanophasenseparation bezeichnet.^[10] Abhängig vom Wassergehalt sind diese Kanäle separiert voneinander, verbunden oder die Struktur wird invertiert, sodass die wässrige Phase die Hauptphase bildet und die mechanische Stabilität verloren geht.^[8,11] Dies zeigt, dass das Wasser-Management der Membran einen entscheidenden Einfluss auf die Effizienz und Funktion der Brennstoffzelle bzw. des Elektrolyseurs hat. Der ideale Wassergehalt ist der Bereich von 0,25 bis 0,50 gew.-%, in dem die Kanäle verbunden sind.^[8] Die Größe dieser Kanäle und der Cluster reichen hierbei von ca. 2 bis 15 nm.^[8,12] Das in diesen Kanälen und Cluster befindliche Wasser gliedert sich in drei Arten, das stark gebundene Wasser an den Sulfonsäuregruppen (nicht gefrierend), das in der Hydrationshülle (gefrierend und gebunden) und freies Wasser im Zentrum der Cluster und in den Kanälen und bildet damit ein Confinement, bestehend aus Nafion und Wasser.^[13] Aufgrund der beiden letztgenannten Arten von Wasser in Nafion[®] ist die Einsatztemperatur sowohl zu geringen als auch zu hohen Temperaturen limitiert, wobei hohe Betriebstemperaturen die Passivierung der Katalysatoren durch Katalysatorengifte minimieren würden.^[11,14] Neben den hohen Herstellungskosten von Nafion[®] ist ebenfalls ein entscheidender Nachteil, dass es sich hierbei um ein perfluoriertes Polymer handelt.^[11] So verfolgt die Europäische Chemikalienagentur für die Material-Gruppe der polyfluorierten Alkyl-Substanzen eine mögliche Einschränkung oder gar ein Verbot für den europäischen Wirtschaftsraum.^[15] Dies würde zur Folge haben, dass Nafion[®] nur noch unter Auflagen oder gar nicht mehr für Brennstoffzellen eingesetzt werden darf.

Aufgrund der genannten Nachteile von Nafion[®] wurden zwei Lösungswege fokussiert. Zum einen wurden Composite-Materialien mit Nafion[®] entwickelt^[16–19], zum anderen hat die Forschung alternative Materialien für die Protonenleitung entwickelt und dahingehend untersucht.^[16,19–22] Mit der Herstellung von Nafion[®]-Composites wird unter anderem das vorliegende Confinement verstärkt, indem organische oder anorganische Materialien eingebracht werden, die stärkere Wechselwirkungen mit Wasser ausbilden, sodass die Protonenleitung auch bei geringerem Wassergehalt stattfinden kann.^[23,24] Des Weiteren werden die mechanischen, thermischen, elektrischen und chemischen Eigenschaften verbessert.^[19,24] Das Einbringen von organischen oder anorganischen Materialien in die Struktur von Nafion kann Inhomogenitäten in der Verteilung der Materialien aufweisen, was zu einer Verschlechterung der mechanischen Eigenschaften, zum Beispiel in Form von

Gasdurchbrüchen in der Membran, führt. Zudem können die Leitungskanäle von Nafion verstopft werden, sodass die Leitfähigkeit herabgesetzt ist.^[18]

Basierend auf dieser Erkenntnis wurden alternative Materialien für die Protonenleitung entwickelt, die kostengünstiger als das bisherige Nafion® mit hoher mechanischer Stabilität, einfacher Verarbeitung und thermischer Stabilität entwickelt. Zu diesen Materialien zählen die sulfonierten aromatischen Polymere wie sulfonierte Polyetheretherketone (sPEEK) oder sulfonierte Polysulfone (sPSU).^[25,26] Da diese weiterhin die Nachteile in der Wasserrückhaltekraft wie Nafion® aufweisen und eine Limitierung der Einsatztemperatur aufgrund Zersetzung zeigten, wurden als nächste Materialgruppe die Hochtemperaturmembranen und Phosphorsäure dotierten Polymere entwickelt.^[18] Bei diesen Materialien, meist auf Polybenzimidazol (PBI)-Basis, konnte aufgrund der Funktionellen-Gruppen im Polymer die Zersetzungs- und Einsatztemperatur erhöht werden, was auf stärkeren Wechselwirkungen des Netzwerks mit dem adsorbierten Wasser und der Säuren beruht. Zudem weisen diese eine bessere CO-Toleranz auf, die auch den Einsatz von Reaktionsgasen mit geringerer Reinheit oder Alternativen zu Wasserstoff ermöglicht.^[27]

Bei den bisherigen Systemen handelte es sich um Composite bestehend aus Polymeren oder reine Polymere. Um die Einsatztemperatur weiter zu erhöhen mit Augenmerk auf die Wasserrückhaltekraft wurden Netzwerke oder 2D-Materialien untersucht, wie metallorganische Gerüstverbindungen (engl.: *metal organic frameworks* (MOFs))^[28–30], Silica-Materialien^[31] oder Graphenoxide (GO)^[16]. All diese Materialien weisen funktionalisierbare Gruppen in ihrer Porosität auf, was ermöglicht, dass die Wechselwirkung zwischen Netzwerk und adsorbiertem Molekül dahingehend verändert werden kann, dass starke Rückhaltekräfte ausgebildet werden können und sich ein Confinement bildet. Zudem sind sie gekennzeichnet durch gerichtete Kanäle für den Ladungstransport, welcher entlang der ionischen Kanäle erfolgt.^[21,31,32] Neuere Forschungen haben neben der reinen Funktionalisierung der Materialien ebenfalls die Nanostrukturierung betrachtet.^[33] So wurde unter anderem mittels der Strukturierung der Materialien das Nanoconfinement oder die intrinsisch oder extrinsisch Leitfähigkeit beeinflusst. Diese Materialien zeigen neben ihrer Kompensation der Einsatzlimitierung, die bei Polymeren auftritt jedoch den Nachteil einer geringen physikalischen oder chemischen Stabilität aufweisen. Eine Kombination der Möglichkeit einer Ausbildung eines Confinements aufgrund der Funktionalisierung von Porenräumen, deren Größe und zudem die Stabilität gegenüber äußeren Einflüssen zeigt die Materialgruppe der porösen organischen Polymere (POP) zu denen unter anderem die kristallinen kovalent-organischen Netzwerke (engl.:

covalent organic frameworks (COFs)) und amorphe Netzwerke wie poröse aromatische Netzwerke (engl.: porous aromatic frameworks (PAFs)) oder auch kovalente Triazin-Netzwerke (engl.: covalent triazine frameworks (CTFs)) gehören.^[22,34–37]

Ziel dieser Arbeit war es, poröse organische Netzwerke bezüglich ihrer Protonenleitfähigkeit zu optimieren. Um der Problematik der Einsatztemperatur entgegenzuwirken, wurde ein nanoporöses Netzwerk der Klasse poröse aromatische Netzwerke gewählt. Dieses Netzwerk ermöglicht die Funktionalisierung des Porenraums aufgrund seiner sehr guten Zugänglichkeit sowie der offenporigen Struktur. Diese Porenstruktur erlaubt das Einbringen von Sulfonsäure Gruppen, die direkt oder mittels eines Spacers an das Netzwerk gebunden sind. Die dargestellten Netzwerke wurden bezüglich ihrer chemischen Zusammensetzung und der erfolgreichen Synthese charakterisiert.

Anhand dieser Netzwerke kann die Untersuchung der wässrigen Protonenleitfähigkeit in einem starken Confinement erfolgen. Um die Leitfähigkeit zu bestimmen, wird Impedanzspektroskopie verwendet. Mittels dieser Methode kann die makroskopische Leitfähigkeit bestimmt werden. Um den zugrundeliegenden Mechanismus der sehr guten Leitfähigkeit aufzuklären, wird Kernspinresonanz-Spektroskopie verwendet. Hierbei wird aufgrund der sehr schnellen Relaxation aufgrund von paramagnetischen Zentren im Netzwerk die Linienform-Analyse und T_1 -Relaxation betrachtet. Diese Kombination aus Impedanz- und Kernspinresonanz-Spektroskopie ermöglicht die Klärung des zugrundeliegenden Mechanismus in Kombination mit der Nanostrukturierung des Porenraums. Diese grundlegenden Erkenntnisse sollen einen detaillierteren Einblick in Netzwerke liefern, die ein starkes Confinement ausbilden und eine potentiell neue Auswertungsmethode für derartige Systeme liefern.

1.1. Poröse aromatische Netzwerke (PAF)

Die Materialklasse der porösen organischen Polymere (POPs) beinhaltet die Gruppe der bereits erwähnten porösen aromatischen Netzwerke (PAFs).^[38] PAFs zeichnen sich durch ihre kovalenten Bindungen und die aromatischen Bausteinen aus.^[39] Die strukturellen Baueinheiten der PAFs erstrecken sich von zweidimensionalen Verknüpfungsbausteinen bis hin zu dreidimensionalen.^[39,40] Sie folgen damit dem von Yaghi *et. al* 2003 beschriebenen Prinzip der retikularen Synthese.^[41] Dies besagt, dass ein gezielter Aufbau von Netzwerken aus vordefinierten, meist starren organischen Bausteinen, erfolgen kann, wenn diese miteinander verknüpft werden zu den vorhergesagten Gittern (*reticulum*). Dieses Prinzip ermöglicht die

gezielte Darstellung von Netzwerken mit vordefinierten Porengrößen und Eigenschaften. Das auf die PAFs transferierte Prinzip der retikularen Synthese ermöglichte die Darstellung von Netzwerken mit einer großen inneren spez. Oberfläche, bis hin zu $5600 \text{ m}^2 \text{ g}^{-1}$ (BET-Oberfläche) für PAF-1^[42], was nahe an der inneren spez. Oberfläche der vorhergesagten Oberfläche einer ideal kristallinen diamantartigen Struktur von PAF-1 ist.^[43] Das zugrundeliegende Prinzip der retikularen Synthese der porösen aromatischen Netzwerke ist ebenfalls in der grafischen Darstellung ersichtlich (Abb. 2a). So werden die Wiederholungseinheiten/Baueinheiten der Netzwerke gezeigt, welche eine Kristallinität nahelegen. Entgegen dieser Darstellung ist die Gruppe der PAFs amorph, was auf der Irreversibilität der C-C-Knüpfungsreaktion basiert.^[43,44] Bei der Reaktion handelt es sich um eine in der Regel katalytisch, kinetisch kontrollierte Reaktion, die zu einer irreversiblen C-C-Bindung führt. So wird das Netzwerk PAF-303, auf welchem diese Arbeit basiert, mittels Suzuki-Kupplung synthetisiert.^[45] Strukturebend bei den katalytischen Reaktionen sind die 2D- oder 3D-Baueinheiten und die Porengröße wird durch die, falls vorhandenen, Linker zwischen den Baueinheiten bestimmt.^[39,40] In dieser Arbeit werden die auf einer tertiären Baueinheit basierenden Netzwerke, insbesondere des quartären Kohlenstoffs, betrachtet. Diese Einheit führt zu einer adamantanartigen Struktur wie sie zum Beispiel PAF-1, PAF-11 sowie PAF-303 besitzen (Abb. 2a und b).^[39,44]

Die Studie zur Synthese des Netzwerks PAF-303 von Rose *et al.*^[45] zeigt, dass die spez. Oberfläche und Bildung der Gerüstverbindung in großer Abhängigkeit zu den verwendeten Prä-Katalysatoren, Pd-Spezies und Ligand, sowie Lösungsmittel während der Synthese stehen. Hierbei wird neben dem Verknüpfungsgrad die Interpenetration des Netzwerks beeinflusst, was zu einer spez. Oberfläche von bis zu $1380 \text{ m}^2 \text{ g}^{-1}$ führt. Die spez. Oberfläche kann neben den verwendeten Synthesebedingungen durch den Linker beeinflusst werden. Die Einführung des zusätzlichen Phenylrings bei PAF-303 führt zu einer Reduzierung der spez. Oberfläche um ca. 70 % im Vergleich zu jener von PAF-1.^[44,45] Wird ein weiterer Phenylring eingeführt ergibt sich eine spez. Oberfläche von $704 \text{ m}^2 \text{ g}^{-1}$ für PAF-11 (siehe Abb. 2b).^[46]

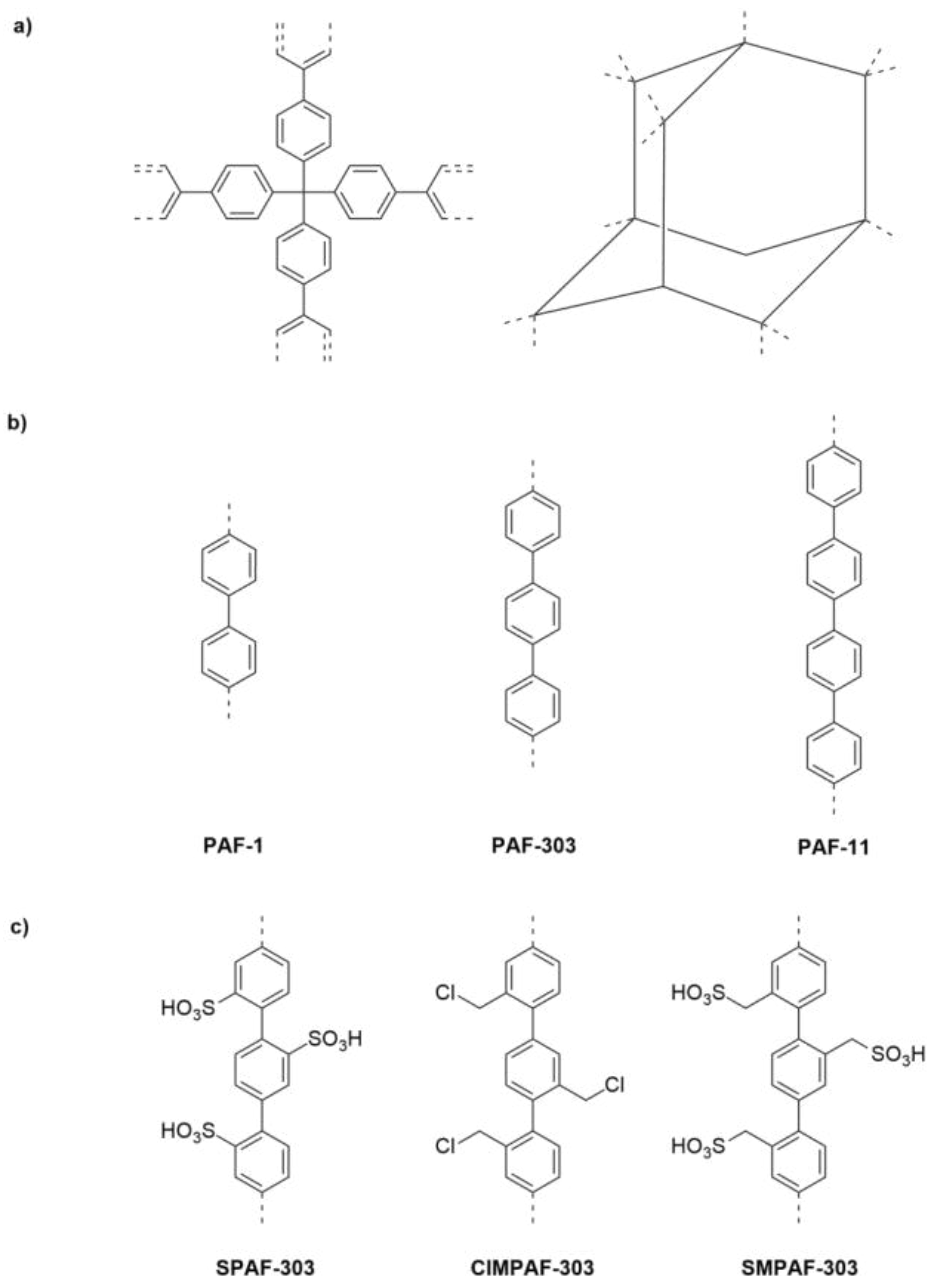


Abb. 2: a) Wiederholungeinheiten des Netzwerks PAF-303. Kleinste idealisierte Wiederholungseinheit (rechts), die bei idealisierter Zusammenführung den Adamantan-Käfig des PAF-303 ergibt. b) Linker-Moleküle, die sich zwischen den quartären Baueinheiten befinden und den Adamantan-Käfig aufspannen. c) Postsynthetisch modifizierte Linker des PAF-303.

Je nach verwendeter Kupplungs-Reaktion ermöglicht diese die Toleranz verschiedener funktioneller Gruppen. Es können mittels der Yamamoto-Ullmann-Kreuzkupplung, die zur Synthese von PAF-1 verwendet wird, Hydroxymethyl-Seitengruppen presynthetisch eingeführt werden.^[47] Die Sonogashira-Hagihara-Kupplungsreaktion ermöglicht bei der C-C-Kreuzkupplung zwischen Aryl-Bromid und Ethin die Einbringung von Carboxylgruppen, die eine anschließende Funktionalisierung des PAF-26-COOH ermöglichen.^[48] Das strukturell ähnliche Netzwerk PAF-70-NH₂ zu PAF-11 wird mittels Suzuki-Miyaura-Kreuzkupplung unter Anwesenheit von Aminogruppen synthetisiert.^[49] Sofern es aufgrund des verwendeten Katalysator-Systems nicht möglich ist funktionelle Gruppen vor der Netzwerkbildung

einzubringen, wird das poröse aromatische Netzwerk postsynthetisch modifiziert. Aufgrund der aromatischen Linker können eine Vielzahl an postsynthetischen Modifikationen durchgeführt werden, wie zum Beispiel die Sulfonierung, Halogenierung, Nitrierung bzw. Aminierung oder das Einfügen von weiteren funktionellen Gruppen wie Methylenhalogenide (Abb. 2c).^[39,50–58] Diese funktionellen Gruppen führen unter anderem bei Anwesenheit während der Netzworkebildung zu Nebenreaktion, welche die Porosität und den Verknüpfungsgrad entscheidend beeinflussen, oder den vorhandenen Katalysator inaktivieren.

Die breiten Variationsmöglichkeiten in der Gerüststruktur, Porosität, funktionellen Gruppen und physikalischen Eigenschaften ermöglichen ein weitgefächertes Einsatzgebiet der PAFs. Diese fanden bereits Anwendung in den Forschungsgebieten der Gassorption, -filterung und -speicherung, Katalyse, Adsorption von Atomen und Molekülen, Sensorik und elektrochemischen Anwendungen.^[39,40,59]

1.2. Mechanismen der Protonenleitung

Zu den möglichen elektrochemischen Anwendungen zählt unter anderem die Verwendung von PAFs als Membran in galvanischen Zellen wie der Brennstoffzelle. In dieser werden in den meisten Fällen Protonen von der Anode zur Kathode transportiert.^[60] Der Transportmechanismus kann je nach verwendetem Elektrolyten anhand unterschiedlicher Mechanismen erfolgen.^[61–63] Im nachfolgenden werden die Mechanismen der wässrigen Protonenleitung genauer beschrieben.

Der Transport der Protonen im wässrigen Medium kann mittels zweier Mechanismen erfolgen, dem Vehikel- und Grotthuß-Mechanismus.^[62] Bei dem erstgenannten können die Protonen sich mit ihrem Trägermolekül H_2O zusammen als Hydroxonium-Ionen (H_3O^+) durch die wässrige Phase bewegen. Dabei sind die Protonen an das Wasser-Molekül chemisch gebunden. Die Trägermoleküle bewegen sich entsprechend in die entgegengesetzte Richtung zu ihren geladenen Ionen.^[64]

Im Gegensatz dazu steht der Grotthuß-Mechanismus. Dieser wird ebenfalls als „Hopping-Mechanismus“ bezeichnet und wurde zu Beginn des 19. Jahrhunderts von Theodor von Grotthuß postuliert und nachgewiesen.^[65] Bei diesem Mechanismus werden Bindungen zwischen dem Proton und dem Donor-Molekül gebrochen und mit dem Akzeptor-Molekül neu gebildet. Die genaue Beschreibung des Mechanismus wurde von *M. Eigen* durchgeführt.^[66,67] Bei dem Grotthuß-Mechanismus ist das Hydroxonium-Ion von drei H_2O Molekülen in der

ersten Solvathülle trigonal umgeben.^[62,68] Diese bilden das Eigen-Ion (H_9O_4^+ -Cluster) wobei das Zundel-Ion (H_5O_2^+) die kleinste Einheit bildet.^[8] Die Wasser Moleküle in der ersten Solvathülle sind wiederum tetragonal umgeben.^[62,68] Diese Wasser-Moleküle bilden die zweite Solvathülle. Damit das Proton des Zentralen Hydroxonium-Ions nun übertragen werden kann, muss die Wasserstoffbrückenbindung zwischen einem Wasser-Molekül aus der zweiten Solvathülle und einem der ersten durch Verkippen des aus der zweiten Solvathülle gebrochen werden. Es bildet sich nun eine Bindung zwischen dem Proton des Hydroxonium-Ions und dem Wasser-Molekül aus der ersten Solvathülle aus und das Proton wird übertragen. Das neu gebildete Hydroxonium-Ion befindet sich nun in einer trigonalen Umgebung, wohingegen das ursprüngliche Hydroxonium-Ion, nun Wasser-Molekül, sich in einer tetraedrischen Solvatationsumgebung befindet.^[62,68]

Neuere Untersuchungen haben gezeigt, dass der Grotthuß-Mechanismus weiter differenziert werden kann. So gibt es neben dem bereits beschriebenen Mechanismus den *packed acid* Mechanismus.^[69,70] Bei diesem Mechanismus erfolgt der Protonen-Transport ebenfalls über Bindungsbruch und -bildung, allerdings ohne Reorientierung des Zundel- und Eigen-Ions. Dieser Mechanismus findet ausschließlich in Systemen statt, die eine hohe Säure- bzw. Ladungsträgerkonzentration aufweisen. Die damit verbundene Säure-Säure-Interaktion ersetzt hierbei die Reorientierung der zweiten Solvathülle. Entgegen der strukturellen Diffusion des Wassers, wie es bei der ursprünglichen Beschreibung des Grotthuß-Mechanismus stattfindet, ermöglicht der *packed acid* Mechanismus eine Protonenleitung selbst im gefrorenen Aggregatzustand, wohingegen die Leitfähigkeit bei der strukturellen Diffusion rapide abnimmt.^[70]

Werden die Wechselwirkungen zwischen dem adsorbierten Wasser und dem Wirt stärker, sodass ein Confinement vorliegt, kann die bisherige Betrachtung der wässrigen Protonenleitung mittels klassischen Vehikel- und Grotthuß-Mechanismus nicht mehr angewandt werden. So zeigten unterschiedliche Studien, dass die Wechselwirkung des Wirts mit den Wasser-Molekülen in Kombination mit der Größe der Kanäle für die Protonenleitung den entscheidenden Faktor bilden.^[71–74] Je nach der Strukturierung der Oberfläche des Materials, das das Confinement ausbildet, liegen unterschiedliche Regime vor. So können stark gebundene Wasser-Moleküle und Hydroxonium-Ionen^[16,75] oder sich abstoßende Wechselwirkungen vorliegen^[74], die eine Diffusion bei sehr niedriger Aktivierungsenergie^[71] bevorzugen. Der Wirt bestimmt ebenfalls den Massentransport im Confinement. So ist abhängig von der Verknüpfung der Leitungskanäle/Poren und deren Größe die molekulare Diffusion gleich oder unterschiedlich zu der makroskopischen Diffusion.^[76] Diese Unterscheidung führte zu der Einführung des

Haven-Verhältnis, das den Unterschied der molekularen und makroskopischen Diffusion/elektrischen Leitfähigkeit beschreibt.^[77] Die aufgeführten Aspekte zeigen, dass die Protonenleitung im Confinement von unterschiedlichen Faktoren abhängig ist. Um den zugrundeliegenden Mechanismus der Leitfähigkeit zu bestimmen, benötigt es deshalb Methoden, welche die molekulare Bewegung detektieren, wie zum Beispiel die Kernspinresonanz-Spektroskopie, und die Impedanz-Spektroskopie, die die makroskopische Leitfähigkeit bestimmt.

1.3. Elektrochemische Impedanzspektroskopie (EIS)

Um den Leitfähigkeitsmechanismus zu untersuchen und die Leitfähigkeit eines Systems zu ermitteln, wird unter anderem die im 19. Jahrhundert entwickelte elektrochemische Impedanzspektroskopie (EIS) verwendet.^[78]

Als Grundlage dient das ohmsche Gesetz (1). Es beschreibt die Proportionalität der Spannung U zur Stromstärke I , die den elektrischen Widerstand R eines Materials definiert. Der definierte Widerstand entspricht einem idealen Widerstand, bei dem die Stromstärke zur Spannung keine Phasenverschiebung aufweist und somit frequenzunabhängig ist.^[79]

$$R = \frac{U}{I} \quad (1)$$

In der Realität findet der ideale Widerstand begrenzt Anwendung. Meist zeigt der Widerstand eine Phasenverschiebung zwischen der Stromstärke und der Spannung, das bedeutet der Widerstand ist frequenzabhängig. Der sich daraus ergebende Widerstand wird als die komplexe Impedanz Z bezeichnet. Die Impedanz wird analog eines zeitabhängigen Widerstandes definiert.^[80] So beschreibt die Formel (2) den Quotienten aus der Spannung U_t und der Stromstärke I_t . Die zeitabhängige Spannung U_t (3) und Stromstärke I_t (4) setzt sich aus der Amplitude der Spannung U_0 und Stromstärke I_0 , der Frequenz ω , der Phasenverschiebung ϕ sowie der Zeit t zusammen. Wird die Impedanz berechnet, so ist es entscheidend, dass die Anregungsspannung so gering wie möglich gehalten wird (1-10 mV). In diesem Spannungsbereich verhält sich das Anregungssignal in erster Näherung linear zum Antwortsignal. Nur in diesem pseudolinearen Bereich kann sichergestellt werden, dass das Antwortsignal, der Strom, linear zum Anregungssignal, der Spannung, gemessen wird und in einer direkt proportionalen Abhängigkeit zueinander stehen.^[78,80,81]

$$Z = \frac{U_t}{I_t} \quad (2)$$

$$U_t = U_0 \cdot \sin(\omega \cdot t) \quad (3)$$

$$I_t = I_0 \cdot \sin(\omega \cdot t + \phi) \quad (4)$$

Die komplexe Impedanz kann mittels Einsetzen der Formel (3) und (4) in das ohmsche Gesetz (2) mit folgender Formel (5) beschrieben werden. Hierbei bildet der Quotient aus U_0 und I_0 die maximale Impedanz Z_0 .

$$Z_t = \frac{U_0 \cdot \sin(\omega \cdot t)}{I_0 \cdot \sin(\omega \cdot t + \phi)} = Z_0 \frac{\sin(\omega \cdot t)}{\sin(\omega \cdot t + \phi)} \quad (5)$$

Mittels der Euler'schen Formel kann die Formel (5) in Formel (6) umgeformt werden.

$$Z_t = Z_0 \frac{e^{i\omega t}}{e^{i(\omega t + \phi)}} \quad (6)$$

Eine weitere Umformung mittels der eulerschen Formel ermöglicht die Beschreibung in Abhängigkeit der Phasenverschiebung (7) und die Aufteilung in einem Realteil Re (8) und den Imaginärteil Im (9).

$$Z_\phi = Z_0(\cos \phi + i \sin \phi) \quad (7)$$

$$Re = Z_0 \cos \phi \quad (8)$$

$$Im = Z_0 \sin \phi \quad (9)$$

Die Gleichung (7) ermöglicht eine vereinfachte Auftragung der Polarkoordinaten in einem Koordinatensystem, in dem der Realteil (8) auf der x-Achse und der Imaginärteil (9) auf der y-Achse (Abb. 3).^[82] Diese Auftragung wird als Nyquist-Plot bezeichnet. Der Phasenwinkel ϕ ist hierbei zwischen den Ursprungsvektor und der x-Achse abgebildet. Der Ursprungsvektor entspricht dem Betrag der Impedanz $|Z|$. Die Berechnung des Phasenwinkels erfolgt mittels Formel (10). Anhand des Pythagoras kann $|Z|$ berechnet werden (11).^[82]

$$\phi = \arctan \frac{Z_{Im}}{Z_{Re}} \quad (10)$$

$$|Z| = \sqrt{Z_{Re}^2 + Z_{Im}^2} \quad (11)$$

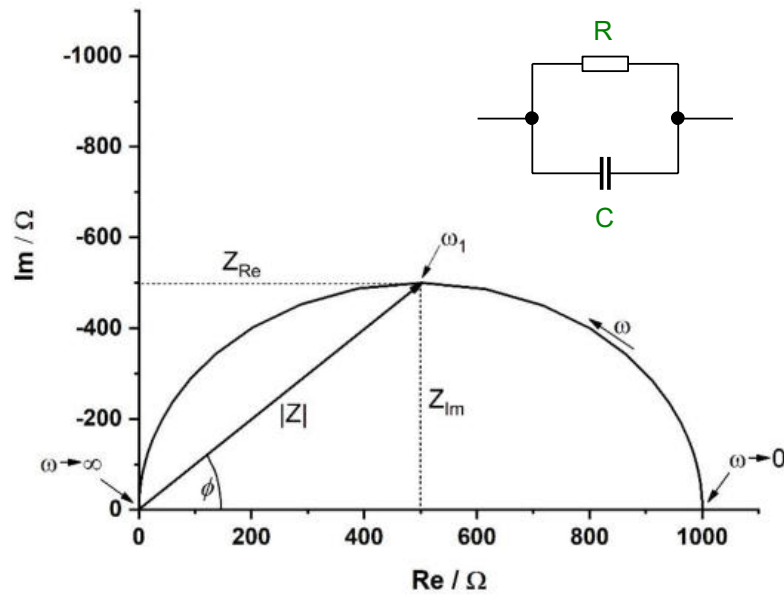


Abb. 3: Nyquist-Plot, indem der Imaginärteil Im gegen den Realteil Re aufgetragen ist. Die Auftragung zeigt Grenzwerte der Frequenz ω wie auch die Resonanzfrequenz ω_1 . Der Ursprungsvektor wird definiert durch den Betrag der Impedanz $|Z|$ und den Phasenwinkel ϕ . Das Inlet zeigt das Ersatzschaltbild bestehend aus einem Widerstand R mit 1000Ω und einem Kondensator mit der Kapazität C von 10 mF , die parallel geschaltet sind. Graph nach Abbildung in Ref. [79] übernommen.

Die Auftragung der Impedanz im Nyquist-Plot liefert in Abhängigkeit der Frequenz für jeden Leitungsmechanismus einen Halbkreis (Abb. 3).^[83] Wird der Halbkreis betrachtet, so zeigt sich, dass keine Aussagen über die Frequenzen getroffen werden können. Es können ausschließlich drei Frequenzen bestimmt werden. $\omega \rightarrow 0$ und $\omega \rightarrow \infty$ sowie an dem höchsten Punkt ω_1 , der definiert ist durch Formel (12), in der C_{CPE} die Kapazität des *Constant Phase Elements* ist.^[80,82]

$$\omega_1 = \frac{1}{R \cdot C_{CPE}} \quad (12)$$

Der Halbkreis kann mittels eines Ersatzschaltbildes simuliert werden. So kann der in Abb. 3 gezeigte Halbkreis mittels eines Kondensators C und Widerstandes R in Parallelschaltung simuliert werden, die in Formel (12) wiedergegeben sind. An den Grenzfällen der Frequenz zeigt sich, dass bei hohen Frequenzen der Kondensator kurzgeschlossen wird und bei niedrigen Frequenzen der Strom ausschließlich über den Widerstand des Ersatzschaltbildes fließt.^[82] Um zu verdeutlichen, dass die Frequenzinformation im Nyquist-Plot nicht enthalten ist, muss Abb. 4 betrachtet werden. Auf der yz -Ebene ist der Nyquist-Plot dargestellt, wohingegen die Frequenz auf die x -Dimension projiziert ist.

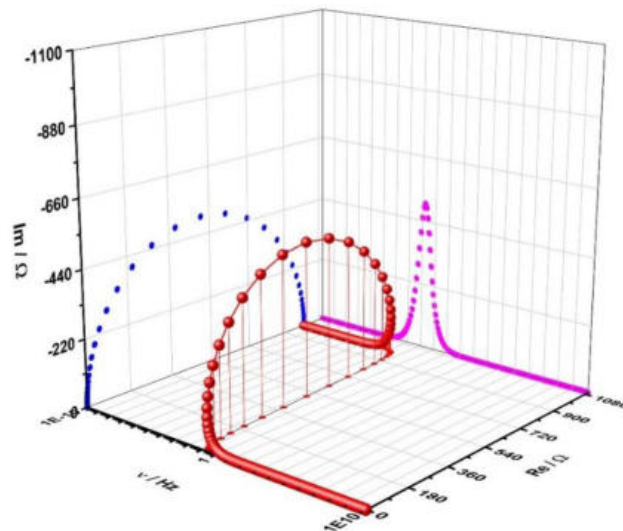


Abb. 4: Dreidimensionale Darstellung der Impedanz (Real- und Imaginärteil) und der Frequenz. Die Auftragung basiert auf dem in Abb. 3 gezeigten Nyquist-Plot. Graph nach Abbildung in Ref. [79] übernommen.

Um Aussagen über die Frequenzabhängigkeit der Impedanz zu erhalten, wird die Impedanz gegen die Frequenz aufgetragen. Diese Auftragung nennt sich Bode-Plot. Neben dieser Darstellung kann der Bode-Plot ebenfalls die Phasenverschiebung gegen die Frequenz zeigen. Diese beiden Auftragungen ermöglichen es, weitere Aussagen über ein System zu treffen und sowie sich überlagernde Leitungsmechanismen voneinander abzugrenzen.

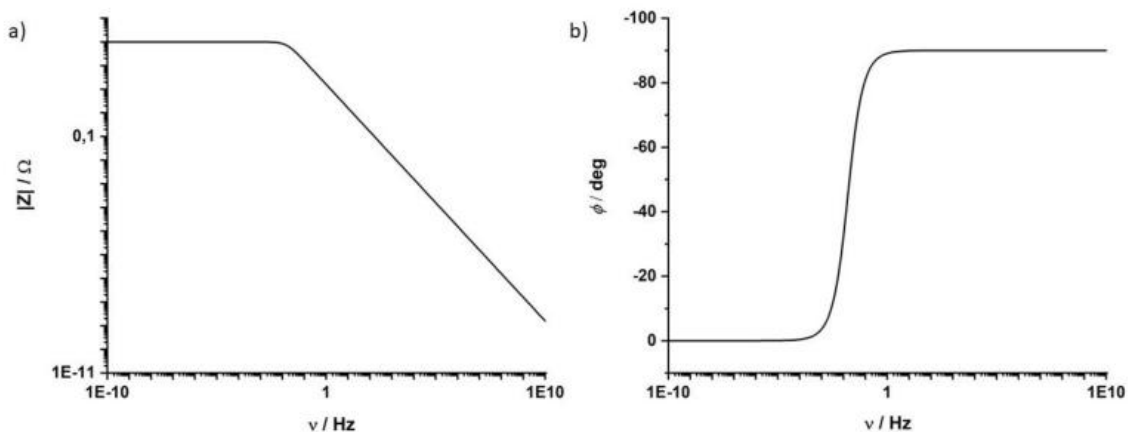


Abb. 5: Auftragung der Bode-Plots basierend auf Abb. 3. a) zeigt den Betrag der Impedanz gegen die Frequenz und b) den Phasenwinkel gegen die Frequenz. Graphen nach Abbildungen in Ref. [79] übernommen.

Die elektrochemische Impedanzspektroskopie liefert die genannten Daten, die anschließend interpretiert und simuliert werden müssen. Für die Simulation der erhaltenen Daten werden neben den bereits beschriebenen Komponenten Widerstand und Kondensator der Induktor L verwendet. Dieser zeichnet sich durch eine Phasenverschiebung von 90° aus und dient als

Gegenspieler zum Kondensator, bei dem die Phasenverschiebung zwischen Spannung und Strom -90° beträgt (Tab. 1).^[78,79,82,84]

Tab. 1: Elektrische Schaltelemente mit ihren physikalischen Eigenschaften, die für die Simulation von EIS-Messungen verwendet werden.^[79,82,84]

<i>Elektrisches Bauteil</i>	Beziehung Strom und Spannung	Impedanz	Phasenverschiebung
<i>Widerstand R</i>	$U(t) = I(t) \cdot R$	$Z = R$	$\Phi = 0$
<i>Induktor L</i>	$U(t) = L \frac{dI(t)}{dt}$	$Z = i \cdot \omega \cdot L$	$\Phi = 90^\circ$
<i>Kapazität C</i>	$I(t) = C \frac{dU(t)}{dt}$	$Z = \frac{1}{i \cdot \omega \cdot C}$	$\Phi = -90^\circ$

Die in einer EIS-Messung erhaltenen Halbkreise geben jeweils ein Bauteil bzw. einen Teil der Probe wieder. Jeder dieser Halbkreise wird mit den elektrischen Bauteilen simuliert. Hierbei werden diese miteinander verknüpft, wobei die kirchhoffsche Regel Anwendung findet.^[85] Diese besagt, dass die Summe aller Ströme als Vektor, betrachtet an einen Knotenpunkt, in Summe sowie die Summe der Spannungen einer Masche, ebenfalls in Vektorbetrachtung, null ergeben muss. Daraus lässt sich die Betrachtung der Summen der Impedanzen in serieller (13) und parallel-Schaltung (14) ableiten.^[82]

$$Z_{Ges} = \sum_{k=1}^n Z_k \quad (13)$$

$$\frac{1}{Z_{Ges}} = \sum_{k=1}^n \frac{1}{Z_k} \quad (14)$$

Anhand der vorgestellten elektrischen Bauteile und der kirchhoffschen Regel können besagte Ersatzschaltbilder konstruiert werden, mit denen die gemessenen Impedanz-Messungen simuliert werden können.^[82] Die Halbkreise, die einen elektrisches Bauteil bzw. einen Anteil der Probe abbilden, können mit Hilfe eines sogenannten RC-Elements simuliert werden. Bei diesem ist ein Widerstand und ein Kondensator parallel zueinander geschaltet. Da in der Praxis meist mehrere Anteile der Probe überlagern, werden im Nachfolgenden zwei RC-Elemente, die in Reihe geschaltet sind, für weitere Erklärungen herangezogen.^[79,82,86,87] Es werden drei Fälle betrachtet (Tab. 2).

Der erste zeigt zwei RC-Elemente, die übereinstimmende Kapazitäten und Widerstände aufweisen (Tab. 2a) u. b)). Hier kann weder in der Nyquist- noch in der Bode-Auftragung nicht mehr auf die zwei RC-Elemente geschlossen werden (Abb. 6a und b). In diesem Fall könnte ebenfalls ein RC-Element mit einem Widerstand von 2 k Ω und einen Kondensator mit der Kapazität von 100 mF angenommen werden. In der Praxis würde dies bedeuten, dass zwischen den beiden elektrischen Bauteilen bzw. den Anteilen der Probe nicht mehr differenziert werden kann.

Das zweite Beispiel zeigt zwei RC-Elemente mit zwei Widerständen, die sich in einer Dekade unterscheiden, bei gleicher Kapazität (Tab. 2c) u. d)). Wird die grafische Darstellung betrachtet, so zeigt sich in der Bode-Darstellung nur in der Vergrößerung, dass zwei RC-Elemente zugrunde liegen (Abb. 6d). Wird die Nyquist-Auftragung betrachtet, so zeigt sich zu Beginn der Auftragung, bei hohen Frequenzen, eine deutliche Abweichung vom Halbkreis, da hier die beiden Halbkreise nebeneinander vorliegen. Der Gesamtwiderstand der Simulation folgt der kirchhoffschen Regel, wobei die Summe der in Reihe geschalteten Widerstände 1,1 k Ω ergibt.

Im dritten Fall beträgt der Unterschied der Kapazität drei Dekaden (Tab. 2e) u. f)). Die Widerstände wurde hierbei gleich gewählt. Die Nyquist-Auftragung weist eine deutliche Differenzierung der beiden Halbkreise auf, wobei keine Überlagerung vorhanden ist (Abb. 6e). Die Bode-Darstellung zeigt eine deutliche Stufe im Verlauf des Betrags der Impedanz gegen die Frequenz (Abb. 6f). Hierbei ist zu beachten, dass durch die doppellogarithmische Darstellung im Bode-Plot eine optische Verzerrung der beiden vorliegenden RC-Elemente zueinander auftritt.

Tab. 2: Werte für die Widerstände und Kapazität die für die RC-Elemente 1 und 2 angenommen werden. Die RC-Elemente sind hierbei in Reihe geschaltet.

Nyquist- u. Bode- Plot	Widerstand R1	Kondensator C1	Widerstand R2	Kondensator C2
a) u. b)	1 k Ω	100 mF	1 k Ω	100 mF
c) u. d)	100 Ω	100 mF	1 k Ω	100 mF
e) u. f)	1 k Ω	0,1 mF	1 k Ω	100 mF

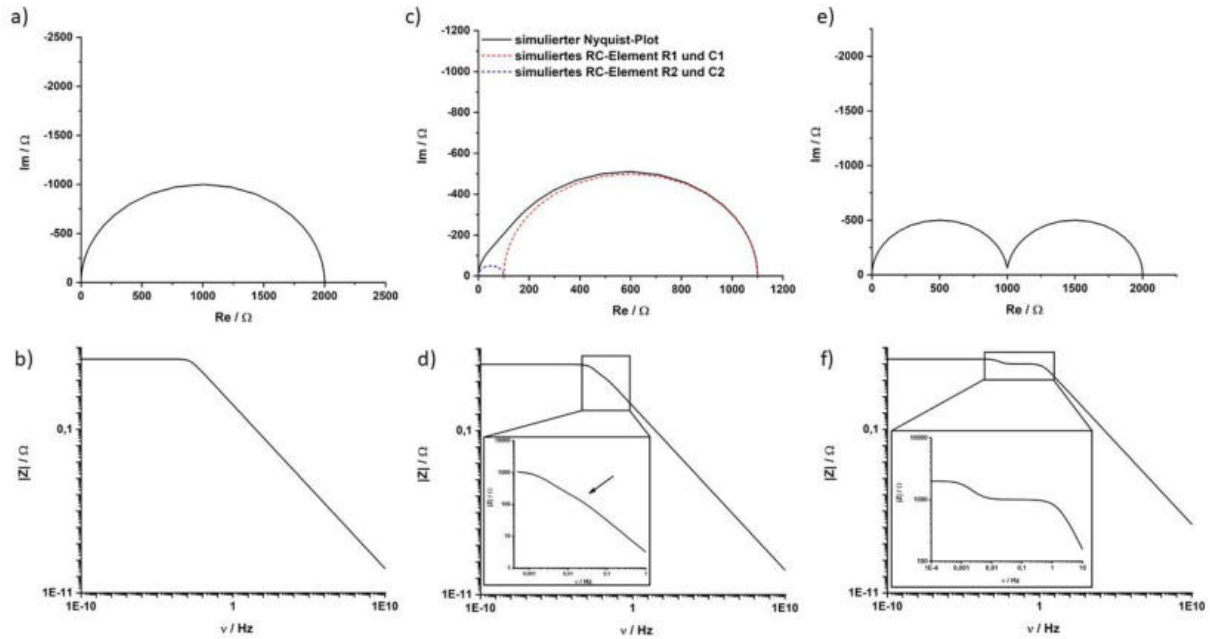


Abb. 6: Nyquist- (a, c, e) und Bode-Auftragung (b, d, f) zweier RC-Elemente die in Reihe geschaltet sind. Für die Simulation der Schaltbilder wurden die Werte aus Tab. 2 in der Software Relaxis 3 simuliert.

Das dritte Beispiel (Tab. 2e und f sowie Abb. 6e und f) zweier getrennt voneinander auftretender Halbkreise liegt vor, wenn zum Beispiel Ladungstransport in einer Probe in unterschiedlichen Distanzen sowie zeitlich deutlich voneinander separiert auftritt. Bei dem ersten und zweiten Beispiel (Tab. 2a-d sowie Abb. 6a-d) findet der Ladungstransport in ähnlichen Distanzen und zeitlichen Größenordnungen statt.

Für jeden Anteil einer Probe kann hierbei eine Leitfähigkeit σ anhand des spez. Materialwiderstandes ρ ermittelt werden. Hierfür wird aus dem entsprechenden RC-Element der Gleichstromwiderstand R ermittelt und mittels der Länge l und der Fläche A , des zu ermittelnden Anteils der Probe, die in der Regel makroskopische Leitfähigkeit mit der Formel (15) bestimmt.^[79]

$$\sigma = \frac{1}{\rho} = \frac{l}{R \cdot A} \quad (15)$$

1.4. NMR-Spektroskopie

Da mittels der Impedanz-Spektroskopie meist die makroskopische Leitfähigkeit einer Probe ausschließlich ermittelt werden kann, benötigt es für die Bestimmung der molekularen Dynamik eine weitere Untersuchungsmethode. Hierfür wird die Kernspinresonanzspektroskopie (engl.: *nuclear magnetic resonance* (NMR)) verwendet.^[88,89]

Die NMR-Spektroskopie basiert auf den magnetischen Eigenschaften von Atomkernen, deren Kernspin I ungleich null ist. In dieser Arbeit werden Wassermoleküle und Oxonium-Ionen untersucht, die Wasserstoff (^1H) enthalten. Wasserstoff besitzt ein Proton und einen Kernspin von $\frac{1}{2}$. Zudem zeigt es eine hohe Sensitivität und Häufigkeit.^[90,91]

Wird ein NMR aktiver Atomkern mit einem magnetischen Moment μ in ein externes Magnetfeld B_0 gegeben, so spalten sich die Energiezustände des Kerns, parallel und antiparallel zum externen Magnetfeld, auf (Abb. 7). Dieser Vorgang ist als Zeeman-Effekt bekannt.^[92]

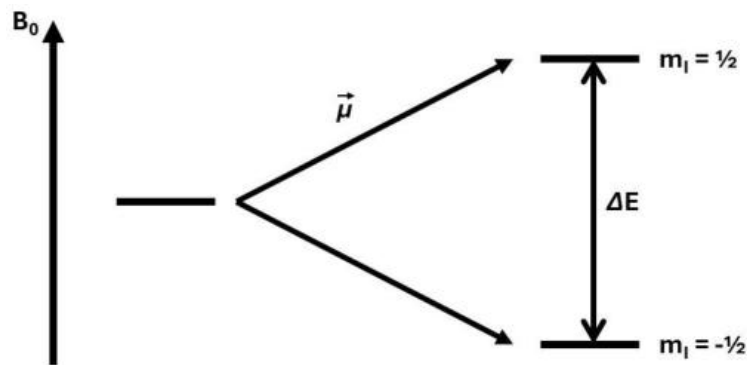


Abb. 7: Darstellung des Zeeman-Effekts anhand von Wasserstoff mit dem Kernspin $\frac{1}{2}$ und dem magnetischen Moment μ im externen Magnetfeld B_0 . Die Energiedifferenz ΔE ist die Energie, die zwischen den aufgespalteten Zuständen vorhanden ist. Abbildung nach Ref. [92].

Die Energiedifferenz ΔE , die sich zwischen den aufgespalteten Zuständen befindet, ist dabei proportional zum magnetischen Feld B_0 und dem gyromagnetischen Verhältnis γ .^[93] Für die Berechnung der Energie der Aufspaltung wird das Produkt aus beiden mit der Konstante $\hbar$ gebildet (16).

$$\Delta E = \gamma \hbar B_0 \quad (16)$$

Wird der Kern mit Radiowellen um die Energie ΔE der Resonanzbedingung angeregt, so werden die Spins aus dem thermischen Gleichgewichtszustand (I) angeregt und es tritt eine Phasenkohärenz der Spins auf (II) (Abb. 8). Hierbei kann die Anzahl der Spins antiparallel zum Magnetfeld maximal die Anzahl der parallelen Spins einnehmen. Dieser angeregte Zustand strebt wieder dazu den Zustand des thermischen Gleichgewichtes zu erreichen.^[92,94–96] Dieser Prozess kann anhand zwei Relaxationsprozesse geschehen. Ist die Spin-Gitter-Relaxation (T_1) gleich der Spin-Spin-Relaxation (T_2), treibt der Relaxationsprozess T_1 die Spin-Spin-Relaxation T_2 . Hierbei kehrt das Spin-System wieder in den thermischen Gleichgewichtszustand zurück, indem angeregte Spins unter Abgabe der Energie an das Gitter in den Ausgangszustand relaxieren (II $\rightarrow$ IV). Bei diesem Prozess geht die Phasenkohärenz verloren. Ist hingegen $T_2 < T_1$ so wird die Phasenkohärenz aufgelöst (II $\rightarrow$ III) und es kann keine Magnetisierung mehr

gemessen werden. Diese Relaxation ist ein rein entropischer Prozess. Die Spins bleiben hierbei in ihren Energieniveaus. Anschließend folgt die T_1 -Relaxation (III $\rightarrow$ IV), bei der die Spins wieder in den thermischen Gleichgewichtszustand (IV) gelangen.^[92,94–96]

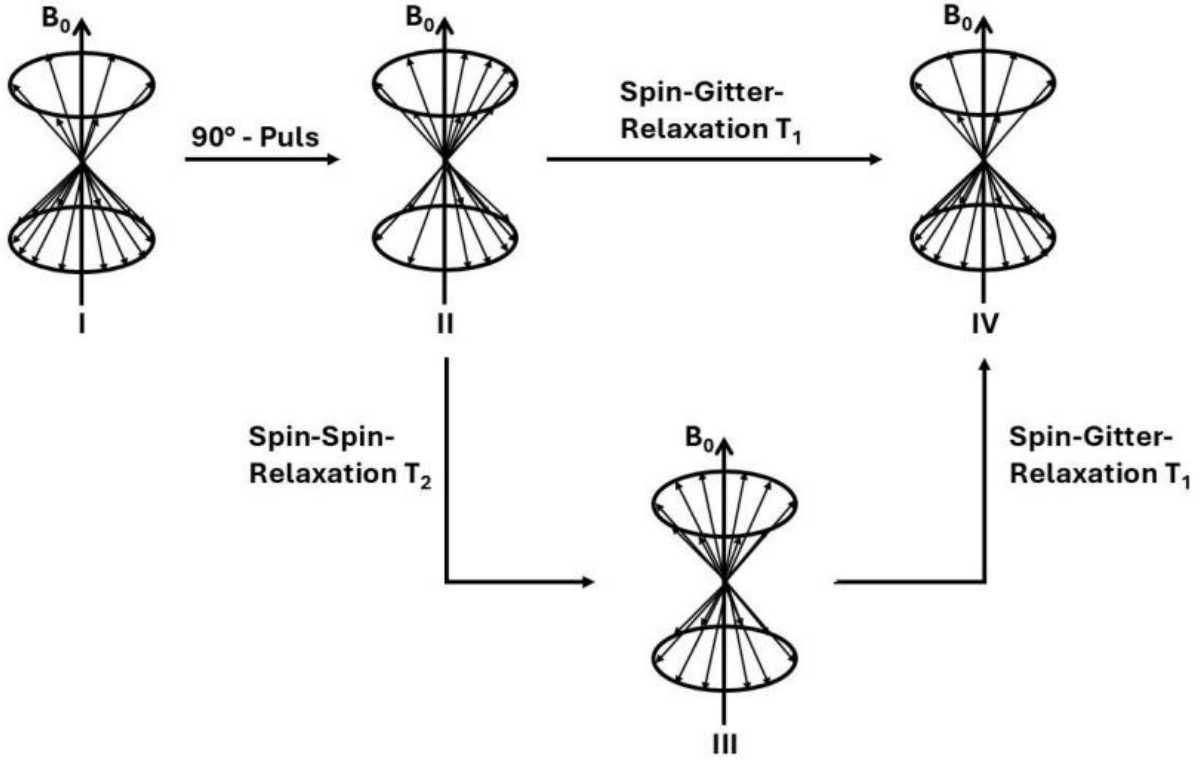


Abb. 8: Verlauf der Spin-Zustände ausgehend aus dem thermischen Gleichgewicht (I), der Anregung mittels 90°-Puls durch die sich die Magnetisierung und Kohärenz ausbildet (II), über die Relaxation T_2 durch die die Kohärenz verloren geht (III) und die T_1 -Relaxation, durch die ebenfalls die Kohärenz verloren geht und die Spins wieder das thermische Gleichgewicht erreichen (IV). Abbildung nach Ref. [94].

Die Spin-Verteilung im thermischen Gleichgewichtszustand (I und IV) lässt sich mit der folgenden Gleichung ermitteln:^[97]

$$\frac{N_\beta}{N_\alpha} = e^{-\frac{\Delta E}{k_B T}} = e^{-\frac{2\mu_B B_0}{k_B T}} \quad (17)$$

Hierbei ist N_β und N_α die Anzahl der parallelen und antiparallelen Spins zum externen Magnetfeld B_0 . k_B ist die Boltzmann-Konstante und T die Temperatur. Werden die magnetischen Momente der einzelnen Spins aus den jeweiligen Zuständen summiert, so ergibt sich die makroskopische Magnetisierung M , die als Antwortsignal gemessen wird. Die gemessene transversale Magnetisierung ist im thermischen Gleichgewicht $M_z = 0$ (I und IV) und im angeregten Zustand II ist diese maximal (Abb. 8). Die Magnetisierung im angeregten Zustand präzisiert dabei mit der Larmor-Frequenz um das Magnetfeld (18).^[96]

$$\omega_0 = -\gamma B_0 \quad (18)$$

Der bereits beschriebene Zerfall der Magnetisierung durch die Spin-Spin-Relaxation T_2 führt zu einem Abfall der zu messenden Magnetisierung, das dem freien Induktionszerfall (engl.: *free induction decay* (FID)) entspricht (Abb. 9).^[96]

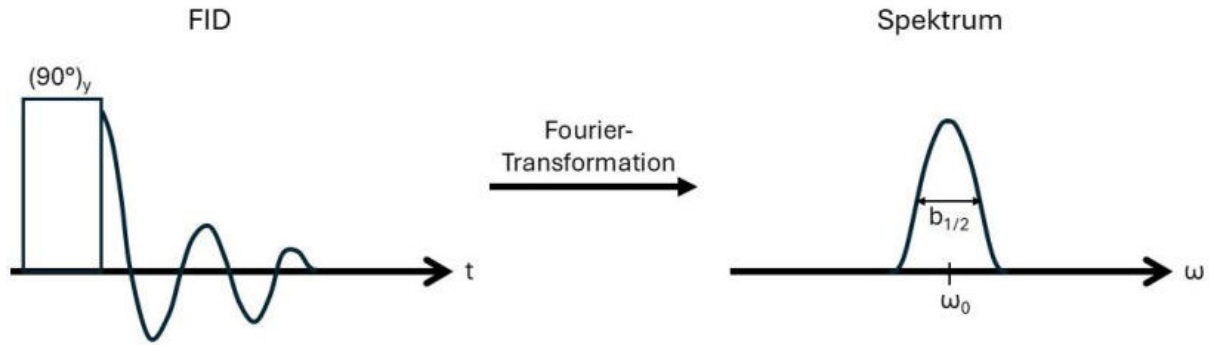


Abb. 9: 90°-Anregungspuls in y-Richtung mit anschließender detektierter transversaler Magnetisierung als Antwortsignal (FID) mit anschließender Fourier-Transformation des Realteils zum Spektrum mit einem on-resonanten Signal und der Halbwertsbreite $b_{1/2}$. Abbildung nach Ref. [91].

Der Abfall der Magnetisierung $M_+(t)$ im FID kann nach den Bloch-Gleichungen, die die Magnetisierung im zeitlichen Verlauf wiedergibt, wie folgt beschrieben werden (19).^[94,95,98] Da während des Zerfall-Prozesses der Magnetisierung keine makroskopische Magnetisierung in Z-Richtung aufgebaut wird, gilt $M_z = 0$.

$$M_+(t) = M_x + iM_y = M_0 e^{-\left(\frac{1}{T_2} - i\Delta\omega\right)t} \quad (19)$$

Der Verlauf der Magnetisierung wird anschließend durch numerische Fourier-Transformation in das komplexe NMR-Spektrum $S(\omega)$ (20) umgewandelt. Das Spektrum besteht hierbei aus einem Absorptions- ($A(\omega - \Delta\omega)$) und Dispersionsteil ($D(\omega - \Delta\omega)$).^[96] Der Absorptionsanteil bildet den Realteil und der Dispersionsteil den imaginären Anteil. Der Absorptionsteil wird für die folgenden Analysen betrachtet und wird als Lorentz-Kurve bezeichnet (vgl. Abb. 9).^[96]

$$S(\omega) = \int_0^\infty M_0 e^{-\left(\frac{1}{T_2} - i\Delta\omega\right)t} e^{-i\omega t} dt = \frac{M_0}{\frac{1}{T_2} - i(\omega - \Delta\omega)} = \frac{M_0 \left(\frac{1}{T_2} - i(\omega - \Delta\omega) \right)}{\left(\frac{1}{T_2} \right)^2 + (\omega - \Delta\omega)^2} \quad (20)$$

Das erhaltene Spektrum beinhaltet in der Linienform der Signale Informationen über die Dynamik und strukturelle Umgebung der einzelnen gemessenen Kerne. Hierfür wird die Linienbreite, die durch die Halbwertsbreite (engl.: *full width at half maximum* (FWHM)) $b_{1/2}$, mit der Beziehung $b_{1/2} = \frac{2\pi}{T_2}$, charakterisiert wird, betrachtet. Diese wird neben Feldinhomogenitäten durch zwei Prozesse, die Spin-Gitter- und Spin-Spin-Relaxation,

beeinflusst. Hierbei sind die beiden Grenzfälle, die freie Bewegung und der starre Festkörper, zu betrachten (vgl. Tab. 3).^[91] Für frei bewegliche niedermolekulare Flüssigkeiten ergibt sich ein sehr schmales Signal, das bedeutet, dass der FID langsam abfällt, wohingegen starre Festkörper aufgrund der unterschiedlichen Ausrichtungen der magnetischen Momente zum äußeren Magnetfeld ein sehr breites Signal liefern, das bedeutet, dass diese eine sehr kurze T_2 -Zeit und einen schnellen Abfall des FIDs besitzen. Aufgrund dessen können anhand der Linienbreite Aussagen getroffen werden, wie die molekulare Dynamik einzelner Moleküle ist.

Tab. 3: Grenzfälle der Linienbreite in Abhängigkeit der Korrelations- und Relaxationszeiten.^[91]

<i>FWHM</i>	Zusammenhang/Bedingungen der Korrelationszeit τ_c und Relaxation	Beispiel	Relaxationszeiten
<i>schmal</i>	$\omega_0 \tau_c \ll 1; \frac{1}{T_1} \propto \tau_c; T_1 = T_2$	niedermolekulare frei bewegliche Flüssigkeiten	10 ms – 10 s
<i>sehr breit</i>	$\omega_0 \tau_c \gg 1; \frac{1}{T_1} \propto \frac{1}{\omega_0^2 \tau_c}; T_1 \gg T_2$	starre Festkörper	T_1 : 1 ms – 10 s T_2 : 10 μ s – 1 ms

Einen weiteren Einblick in die molekulare Dynamik liefert die T_1 -Relaxation. Für isotrope Rotationsdiffusion dipolar gekoppelte Spinpaare, wie sie in klassischen Flüssigkeiten auftreten, kann mit dem Abstand r zwischen diesen mittels der Bloembergen-Purcell-Pound-Theorie (BPP-Theorie)^[96,99,100] (21) anhand der T_1 -Relaxationszeiten die Aktivierungsenergie E_A der Rotationsbewegung ermittelt werden (22). Um diese zu erhalten, wird die Korrelationszeit τ_c bestimmt. Hierzu muss das Integral der Fourier transformierten exponentiellen Autokorrelationsfunktion $G(\tau)$ berechnet werden, welches die spektrale Dichte $J(\omega_0)$ definiert. Die Korrelationszeit τ_c kann anhand der Exponentialfunktion nach Arrhenius mit dem präexponentiellen Faktor τ_0 und der Aktivierungsenergie in Abhängigkeit der Temperatur T wiedergegeben werden. Hierzu wird (22) in (21) eingesetzt.^[101] Anhand der resultierenden Funktion ist es möglich die Aktivierungsenergie der schnellen Rotationsbewegung in Flüssigkeiten durch Fitting der T_1 -Daten zu bestimmen.

$$\frac{1}{T_1} = K \gamma^4 I(I+1) \frac{1}{r^6} [J(\omega_0) + 4J(2\omega_0)] \quad (21)$$

$$J(\omega) = \int_0^\infty G(\tau) e^{-i\omega\tau} d\tau = \frac{\tau_c}{1 + \omega^2 \tau_c^2} = \frac{\tau_0 e^{\frac{E_A}{RT}}}{1 + \omega^2 \tau_0^2 e^{\frac{2E_A}{RT}}} \quad (22)$$

Diese Betrachtung gilt nicht mehr für heterogene Systeme, wie sie zum Beispiel bei Winterstein *et. al*^[102] beschrieben sind. In diesem System sind paramagnetische Zentren vorhanden. Diese Zentren bewirken, dass die Translationsbewegung der dominierende Anteil am

Korrelationsverlust der spektralen Dichte ist. Dies führt dazu, dass die erhaltene Formel der T_1 -Relaxation in Abhängigkeit des Integrals der spektralen Dichte der translatorischen Bewegung nur noch numerisch gelöst werden kann. Dieser Zusammenhang ermöglicht, dass anhand von T_1 -Messungen eine Aussage über die Aktivierungsenergie der molekularen Diffusionsbewegung getroffen werden können.

Um die T_1 -Relaxationszeiten zu ermitteln, wird die in dieser Arbeit verwendete *Inversion-Recovery*-Methode verwendet.^[96,98,103] Durch einen 90°_x -RF-Puls wird die Magnetisierung in z-Richtung erhalten (siehe Abb. 10). Anschließend erfolgt ein 180° -RF-Puls in x-Richtung, sodass die Magnetisierung entlang der z-Achse invertiert wird. Nachfolgend wird die variable Wartezeit τ gewartet. In dieser Zeit relaxiert die Magnetisierung mittels T_1 -Relaxation. Nachfolgend wird die Magnetisierung mittels eines 90° -Pulses wieder in die xy-Ebene gekippt, sodass das Antwortsignal detektiert werden kann.^[96,98]

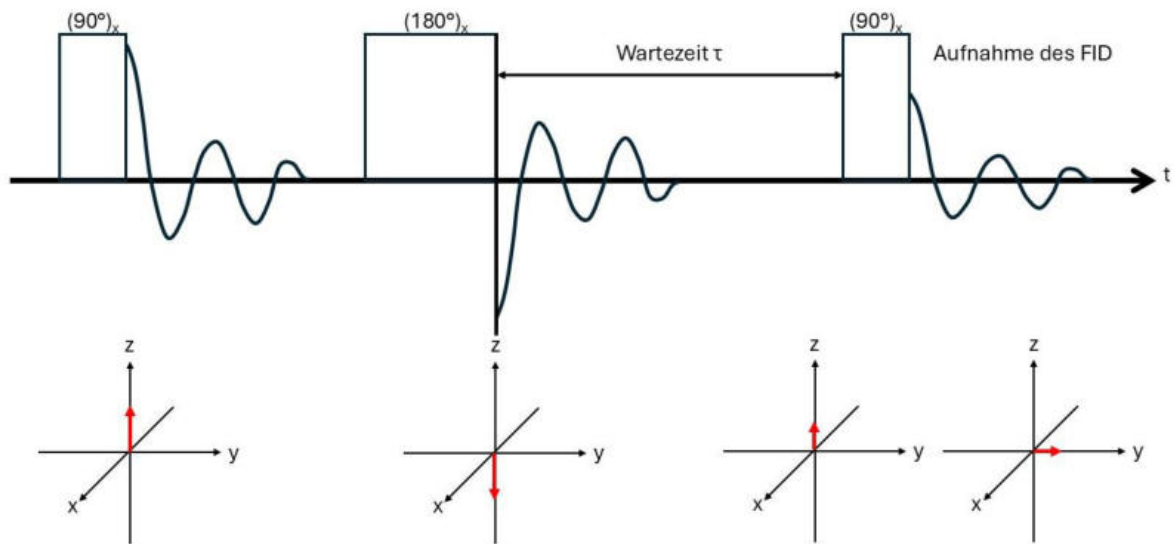


Abb. 10: Pulssequenz des Inversion-Recovery-Experiments mit Verlauf der Magnetisierung während des Experimentes. Abbildung nach Ref. [96].

Die Signalintensität bildet sich hierbei als Abhängigkeit der Wartezeit (23). Durch Variation der Wartezeit wird eine Aufbaukurve der Magnetisierung erhalten, durch die die T_1 -Relaxationszeit bei der jeweiligen Temperatur bestimmt werden kann.^[98] Formel (23) beschreibt ein System, indem ausschließlich eine T_1 -Relaxation vorliegt.

$$M_z(\tau) = M_0 \left(1 - \frac{M_0 - M_0^z}{M_0} e^{-\frac{\tau}{T_1}} \right) \quad (23)$$

Sind in einem System unterschiedliche T_1 -Relaxationen vorhanden und wird die Wartezeit τ lang genug gewählt, sodass alle Moleküle vollständig relaxieren können, so ergibt sich die

Magnetisierung $M_z(\tau)$ aus Summe der einzelnen T_1 -Relaxationsanteile unter Berücksichtigung ihrer Anteile x an der Gesamtheit (24).

$$M_z(\tau) = M_0 \left(1 - \sum x \frac{M_0 - M_0^{zi}}{M_0} e^{-\frac{\tau}{T_{1i}}} \right) \quad (24)$$

Eine solche Addition einzelner Spin-Gitter-Relaxationen tritt unter anderem auch in einem Confinement auf. Dabei handelt es sich um poröse Systeme, wobei es zu unterschiedlichen Relaxationszeiten und Dynamiken im Porenraum kommen kann.^[104–106] Hierbei kann ebenfalls ein schneller Abfall des FIDs auftreten. Dies beruht auf unterschiedlicher Effekte wie der eingeschränkten Diffusion, eines multiexponentiellen FID-Abklingprozesses oder verstärkter Signalinhomogenitäten durch Adsorption an Oberflächen und unterschiedlichen chemischen Umgebungen.^[101,107,108] Neben einer Verkürzung der T_2 -Relaxation kann ebenfalls eine Verkürzung der T_1 -Relaxation sowie des Selbstdiffusionskoeffizienten auftreten.^[101,107,109] Hierbei ist die Stärke des gebildeten Confinements entscheidend, was vor allem durch die chemische Struktur und Größe der Poren hervorgerufen wird.

2. Synopsis

Die vorliegende Dissertation basiert auf zwei Publikationen und einem Manuskript. Das nanoporöse aromatische Netzwerk PAF-303 bildet die Basis dieser Arbeit. Es ermöglicht aufgrund seiner offenporigen adamantanartigen Porenstruktur ein ideales System für postsynthetische Modifizierungen. Es wurden Sulfonsäuregruppen in das Netzwerk eingebracht, um die Gerüststruktur hydrophiler zu gestalten, sodass die Wasseradsorption erhöht werden kann. Dies geschah mittels etablierter Syntheserouten wie auch einer neuen postsynthetischen mehrstufigen Umsetzung, was in beiden Fällen zu neuen Netzwerken führte. Die addierten Sulfonsäuregruppen dienen zudem als Protonendonatoren, die die Ionen-Austausch-Kapazität (engl.: *ion exchange capacity*, IEC) sowie die Hydrophilie des Netzwerks erhöhen. Das aufgrund der Nanoporosität und starken Wechselwirkungen zwischen dem Netzwerk und Wasser ausgebildete Confinement gilt es anschließend auf die Protonenleitfähigkeit und den zugrundeliegenden Mechanismus zu untersuchen. Hierfür wurden etablierte Messmethoden durchgeführt und diese auf neue Weise zueinander in Bezug gesetzt, was einen detaillierteren Einblick in die den Aufbau des Netzwerks und die Protonenleitung lieferte.

In der Publikation „*Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework*“ werden die Netzwerke SPAF-303_x postsynthetisch mit der etablierten Gassulfonierung mittels gasförmigen SO₃ dargestellt. Hierbei wurden drei Sulfonierungsgrade x von 30 %, 50 % und 80 % realisiert. Anschließend wurden ihre chemische Zusammensetzung sowie die Struktur und Anordnung der Sulfonsäuregruppen charakterisiert. Die makroskopische Protonenleitung wurde in Abhängigkeit des Wassergehaltes mittels Impedanzspektroskopie untersucht, wobei die Gesamtleitfähigkeit von bis zu 1 S cm² gemessen werden konnte. Um diese herausragende Leitfähigkeit detaillierter zu verstehen, wurde im weiteren Verlauf der Arbeit der Mechanismus unter 100 % Luftfeuchtigkeit, was einer vollständigen Füllung der Pore entspricht, auf molekularer Ebene untersucht. Aufgrund von paramagnetischen Zentren in den Netzwerken konnte anhand der Messung von Spin-Gitter-Relaxationszeiten die translatorische Leitfähigkeit ermittelt werden. Es wurde gezeigt, dass diese mit Diffusionskoeffizienten übereinstimmen, die aus statischen Feldgradienten (engl.: *static-field gradient*, SFG) -Messungen ermittelt wurden. So war es möglich ebenfalls für sehr kurze Relaxationszeiten, bei denen keine SFG-Messungen möglich waren, Diffusionskoeffizienten zu ermitteln. Die Kombination aus Kernspin-Resonanz- und Impedanzspektroskopie, die die mikroskopischen und makroskopischen

Leitfähigkeiten und die zugrundeliegenden Aktivierungsenergien beschreiben, ermöglicht es den Leitungsmechanismus in einem starken Confinement aufzuklären.

Das auf den gleichen Netzwerken basierende Manuskript „*Understanding of Proton Conduction in Confinement of SPAF-303*“ ergänzt die Publikation „*Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework*“. In dieser Arbeit werden unter den relativen Luftfeuchtigkeiten 33 und 67 % RH, die nur teilweise gefüllten adamantanartigen Poren untersucht. Hierfür wurden die beschriebenen Methoden der Impedanz- und Kernspin-Resonanz-Spektroskopie angewandt und deren Anwendung auf das deutlich stärkere Confinement als bei 100 % RH gezeigt. Dies zeigte einen deutlichen Unterschied zwischen den ermittelten mikroskopischen und makroskopischen Leitfähigkeiten und deren limitierten Abhängigkeit zueinander in einem starken Confinement. Anhand dieser Aussagen konnte der Einfluss des Netzwerks auf die Protonenleitfähigkeit in Abhängigkeit des Füllgrades der Poren beschrieben werden.

Die Publikation „*Thermodynamically Stable Functionalization of Microporous Aromatic Frameworks with Sulfonic Acid Groups by Inserting Methylene Spacers*“ basiert auf dem Netzwerk SMPAF-303 und stellt eine Weiterentwicklung des Netzwerks SPAF-303 dar. Bei den Netzwerken der Gruppe SPAF sind die Sulfonsäuregruppen direkt an das aromatische Grundgerüst gebunden. Diese Bindung ist reversibel und kann unter Umständen zur Abspaltung der Sulfonsäuregruppe zu Schwefelsäure führen. Hierbei galt es die Sulfonsäuregruppen dauerhaft zu immobilisieren, sodass die Vorteile des Netzwerks SPAF mit der irreversiblen Anbindung der Sulfonsäuregruppen kombiniert werden kann. Ziel war es, die Sulfonsäuregruppen mittels einer Methylen-Gruppe an das aromatische Grundgerüst zu binden. Die Darstellung erfolgte hierbei mittels einer zweistufigen postsynthetischen Umsetzung ausgehend von PAF-2. SMPAF-303 wurde anschließend auf seine chemische Zusammensetzung und Struktur untersucht, wobei besonderes Augenmerk auf die kovalente Bindung der Sulfonsäuremethylen-Gruppen an das nanoporöse Netzwerk gelegt wurde. Dieses Netzwerk soll aufgrund seiner Eigenschaften und dem chemischen Aufbau eine Grundlage für die Weiterentwicklung poröser aromatischer Netzwerke, die ideal abgestimmt für den Einsatz als protonenleitendes Material sind, sein.

2.1. Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework

Die Arbeit befasst sich mit der Darstellung und Charakterisierung eines Netzwerks für die Anwendung als protonenleitendes Material sowie der Beschreibung des zu Grunde liegenden Leitungsmechanismus. Das in der Publikation beschriebene PAF-2 ist ebenfalls in der Literatur beschrieben unter PAF-303 und wird im Nachfolgenden auch als dieses bezeichnet. Ausgehend von dem linearen Linker Benzen-1,4-diborsäure und dem dreidimensionalen Linker Tetrakis-(4-bromophenyl)methan wurde das nanoporöse Netzwerk PAF-303 mittels Suzuki-Kupplungsreaktion dargestellt. Die erfolgreiche Darstellung konnte mittels NMR-Spektroskopie, Elementaranalyse und energiedispersiver Röntgen- (engl.: *energy dispersive X-ray* (EDX)) Spektroskopie bestätigt werden. Das dargestellte PAF-2 zeigte einen hohen Vernetzungsgrad von 90 %. Zudem wiesen die Analysen in dem Netzwerk Spuren des Katalysators von 0,02 at.-% für Pd und 0,08 at.-% Fe nach. Diese Verunreinigungen waren fest in die Struktur des Netzwerks gebunden und konnten nicht extrahiert werden. Anschließend wurde das Netzwerk postsynthetisch mittels Gasphasensulfonierung mit SO₃ zu SPAF-303 umgesetzt (Abb. 11). Es wurden drei Sulfonierungsgrade von 30 %, 50 % und 80 % erhalten. Dies erhaltenen Sulfonierungsgrade wurden dabei mittels Titration, Elementaranalyse und EDX-Spektroskopie bestimmt, wobei eine homogene Verteilung der Sulfonsäuregruppen über das Netzwerk auf makroskopischer Verteilung bestätigt werden konnte. Anhand von Weitwinkel-Röntgenstreuung-Experimenten (engl.: *wide-angle X-ray scattering*, WAXS) konnte nachgewiesen werden, dass bei 50 % Sulfonierungsgrad innerhalb einer Pore ebenfalls eine homogene Verteilung der Sulfonsäuregruppen auftritt und es zu keiner Clusterung dieser kommt.

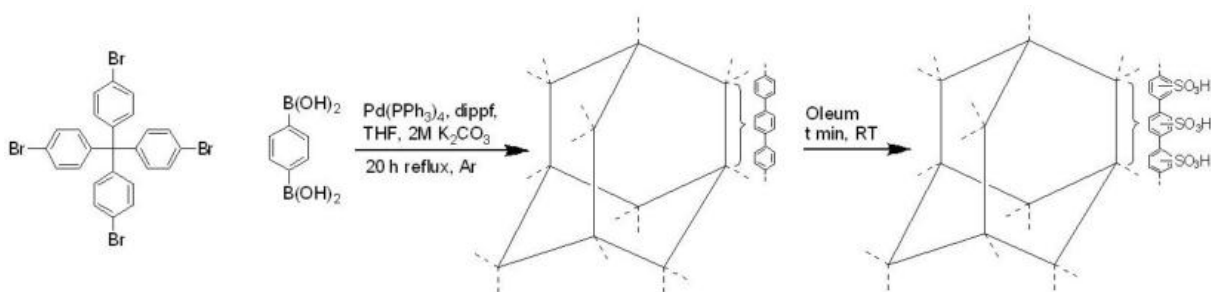


Abb. 11: Synthese-Schema von SPAF-303. Ausgehend von den Edukten Tetrakis-(4-bromophenyl)methan und Benzen-1,4-diborsäure die mittels Kupplungsreaktion PAF-303 bilden. Anschließend erfolgt die Einführung von Sulfonsäuregruppen mittels Gasphasensulfonierung des gebildeten Netzwerks. [Adaptiert unter dem Aspekt der Lizenz CC BY-NC-ND 4.0 aus der Referenz^[102]]

Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework

Des Weiteren wurden die Netzwerke mittels Argon-Physisorption auf ihre innere Oberfläche untersucht. PAF-303 wies eine BET-Oberfläche von $1692 \text{ m}^2 \text{ g}^{-1}$ mit einem Mikroporen-Anteil von 48 % und ein Porenvolumen von $1,263 \text{ cc g}^{-1}$ auf. Nach der Sulfonierung wurde ein drastischer Rückgang der Argon-Aufnahme beobachtet. So zeigte das Netzwerk bei 80 % Sulfonierung nur noch $124 \text{ m}^2 \text{ g}^{-1}$ und ein Porenvolumen von $0,198 \text{ cc g}^{-1}$. Ebenfalls reduzierte sich der Mikroporen-Anteil auf 19 %. Wurde das Adsorptiv durch Wasser ersetzt, so war bei den sulfonierten Netzwerken eine hohe H_2O -Aufnahme ersichtlich, die entgegen der Argon-Physisorption steht. In Kombination mit dynamischer Differenzkalorimetrie (engl.: *differential scanning calorimetry* (DSC)) und Rasterelektronenmikroskopie (engl.: *scanning electron microscopy* (SEM)) unter definierter Luftfeuchtigkeit konnte nachgewiesen werden, dass das Wasser die attraktiven Wechselwirkungen zwischen den Sulfonsäuregruppen schwächt und sich zwischen diese einlagert. Diese Einlagerung zwischen den Sulfonsäuregruppen in den Porenraum führt zu einer makroskopischen Zunahme des Volumens der Probe. Aufgrund der starken Wechselwirkungen zwischen den Wassermolekülen und den Sulfonsäuregruppen in Verbindung mit den kleinen Porenräumen zeigt das Wasser eine hohe Rückhaltekraft im Netzwerk und bildet mit dem Netzwerk ein Confinement aus. So war es möglich ab einem Sulfonierungsgrad von 50 % das Porenvolumen des Netzwerks PAF-303 wiederherzustellen.

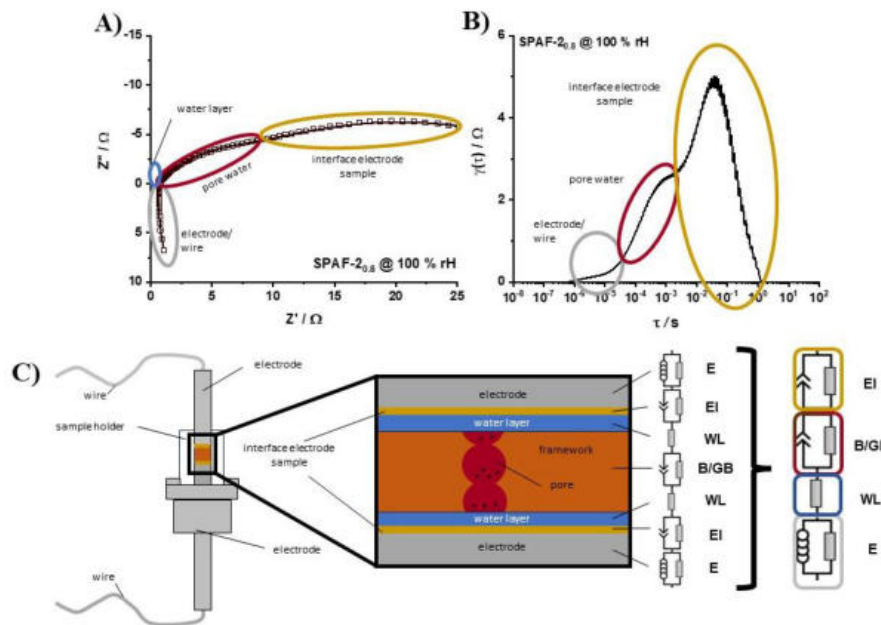
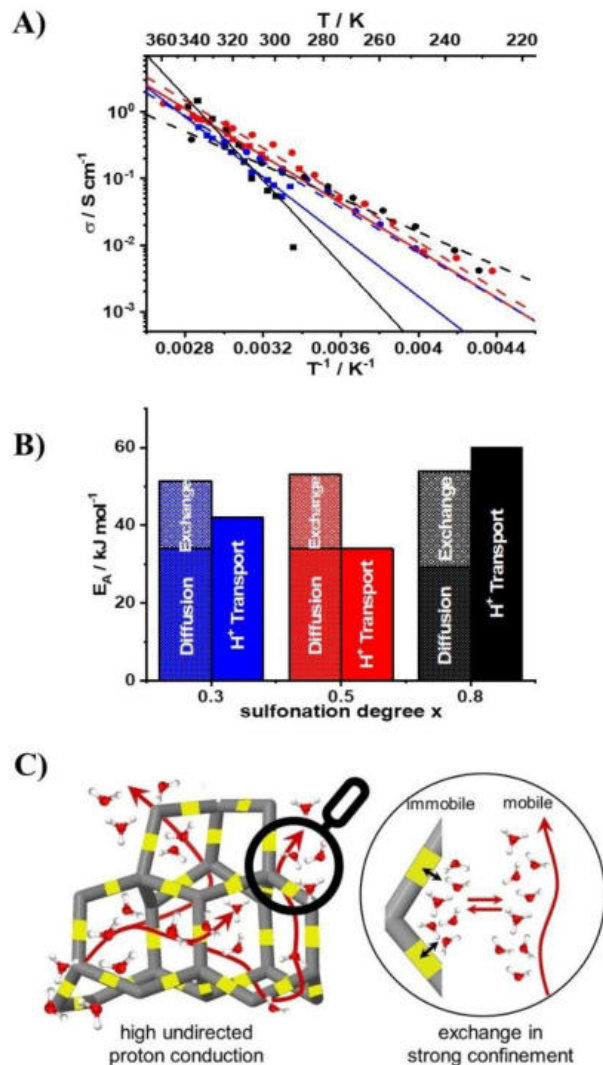


Abb. 12: Impedanz-Spektroskopie Messungen bei 303 K von SPAF-303_{0,8} bei 100 % RH(A), Relaxationszeiten berechnet aus der Impedanz-Spektroskopie Messung mittels RelaxisIS 3 (B) und schematische Darstellung des Messaufbaus mit Vergrößerung der Probe mit Erklärung des Ersatzschaltbildes (C). Der Farbcode zeigt in grau die Kabel (E), in blau die Wasserschicht an der Grenzfläche der Probe zur Elektrode (WL), in Rot die Probenbestandteile des Bulks und der Korngrenzfläche (B/GB) sowie in Gelb die Elektrodengrenzfläche (EI).

Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework

Um die makroskopische Leitfähigkeit der Probe zu ermitteln, wurden Impedanz-Spektroskopie Messungen durchgeführt. Die davon erhaltenen Nyquist-Auflagen (Abb. 12A) zeigten neben den Bestandteilen des Messaufbaus die Probe. Hierbei konnte anhand der Relaxationszeiten (Abb. 12B) eine Zuordnung der Probenbestandteile, wie zum Beispiel Leitung im Bulk oder über Korngrenzen, erfolgen. Anhand der ermittelten Relaxationszeiten konnte ein Ersatzschaltbild für die Proben generiert werden (Abb. 12C), was den Aufbau und



hydrophilen Stellen (gelb), nahe der Sulfonsäuregruppen, dargestellt. Die Vergrößerung zeigt den Austausch beider Regime schematisch dargestellt. [Übernommen unter den Richtlinien der Lizenz CC BY-NC-ND 4.0 der Referenz^[102]]

Einblick in die Leitungsmechanismen der Proben wiedergibt. Die aus diesen ermittelten Ersatzschaltbilder bestimmte Gleichstromleitfähigkeit für den Bulk-Widerstand gab die makroskopische Leitfähigkeit wieder. Die Sulfonierung bewirkte einen deutlichen Anstieg der Leitfähigkeit bis 1 S cm^{-1} bei 100 % RH und einer Protonenaustauschkapazität von 6 mequiv g^{-1} (SPAF-303_{0.8}) (Abb. 13A). Dabei bildet das adsorbierte Wasser in der offenen Porenstruktur eine kontinuierliche Phase, was durch das bereits beobachtete Regeneration des Porenraums bestätigt wurde. Durch Linienformanalyse der ^1H NMR-Spektren in Kombination mit T_1 -sowie SFG-Messungen von Protonen der Gerüststruktur SPAF-303 wurden zwei Regime für das adsorbierte Wasser ausgemacht. Zum einen gibt es ein Reservoir in der Pore (mobile Spezies) und Wassermoleküle, die aufgrund starker Wechselwirkungen an die Porenwände bzw. Sulfonsäuregruppen gebunden sind. Diese zwei Regime stehen im ständigen

Abb. 13:A) Leitfähigkeiten von SPAF-303 mit den Sulfonierungsgraden 30 % (blau), 50 % (rot) und 80 % (schwarz) bei 100 % RH ermittelt aus den Impedanz- (Quadrat) und aus ^1H SFG NMR Messung für 30 % und 80 % Sulfonierungsgrad (Kreise). Für den Sulfonierungsgrad 50 % wurden die Daten anhand T_1 -Relaxationszeiten und Nernst-Einstein-Beziehung ermittelt. Die Linien dienen als Hilfslinien um den Verlauf der Leitfähigkeit verdeutlichen. B) Gegenüberstellung der Aktivierungsenergien aus den NMR-Leitfähigkeitsmessungen und dem Austausch der beiden Regime gegen die Aktivierungsenergie ermittelt aus den Impedanz-Messungen. C) Schematische Darstellung der Protonenleitung durch das Netzwerk. SPAF-303 ist in idealisierter Form mit hydrophoben (grau) und

Austausch zueinander, wobei die mobile Spezies mit zunehmender thermischer Energie zunimmt. Zudem konnte mittels statischer Feldgradienten NMR-Spektroskopie (engl.: *static-field gradient* (SFG)) bei den Netzwerken SPAF-303_{0,3} und SPAF-303_{0,8} die Eigendiffusion D bestimmt werden, die um zwei Dekaden größer ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) war als bei adsorbiertem Wasser in porösen Materialien mit Porengröße von 0,74 – 5,4 nm. Für das Netzwerk SPAF-303_{0,5} war es aufgrund der kurzen Spin-Gitter-Relaxationszeit ($< 1 \text{ ms}$) nicht möglich den Diffusionskoeffizienten mittels SFG-Messungen zu bestimmen. Die paramagnetischen Verunreinigungen ermöglichten es mittels Bestimmung der Spin-Gitter-Relaxationszeit die Translation der Protonen relativ zu den statischen paramagnetischen Zentren zu ermitteln. Die so ermittelten hohen Diffusionskoeffizienten sind in Übereinstimmung mit den Daten, die aus SFG-Messungen ermittelt wurden. Die bestimmten Diffusionskoeffizienten bestätigten die offenporige Struktur des Netzwerks mit der kontinuierlichen wässrigen Phase, sodass eine ungehinderte Diffusion nach der Nernst-Einstein-Beziehung erfolgen kann. Dies wird zudem bestätigt durch die Übereinstimmung mit der makroskopischen Leitfähigkeit, bestimmt durch Impedanz-Spektroskopie (Abb. 13A). Anhand des Vergleichs der Aktivierungsenergien aus den NMR- und den Impedanz-Messungen konnte die Abhängigkeit der makroskopischen Leitfähigkeiten von den der mikroskopischen Leitfähigkeiten bestimmt werden (Abb. 13B). So war für die Sulfonierungsgrade 30 % und 80 % ersichtlich, dass die Leitfähigkeit sowohl von der Diffusion als auch vom Austausch der mobilen und immobilen Wasser-Phase bestimmt wird (Abb. 13C). Das Netzwerk SPAF-303_{0,5} nimmt hierbei eine herausragende Stellung gegenüber den anderen Sulfonierungsgraden ein. Durch die alternierende und gleichmäßige Anordnung der Sulfonsäuregruppen am Netzwerk (Abb. 13C), wie es bereits durch die WAXS-Messung gezeigt wurde, sorgt dafür, dass die makroskopische Leitfähigkeit durch die Aktivierungsenergie der molekularen Diffusion bestimmt wird. Dies lieferte ein neues Verständnis für die Leitfähigkeit in porösen Netzwerken, dass die Struktur sowie die Nanostrukturierung der Poren einen entscheidend größeren Einfluss auf die Leitfähigkeit haben als die Ladungsträgerkonzentration selbst.

2.2. Understanding of Proton Conduction in Confinement of SPAF-303

Basierend auf den Erkenntnissen der vorangegangenen Publikation^[102] wurde das Manuskript verfasst, um einen tieferen Einblick in die Abhängigkeit der Leitfähigkeit und dem zugrundeliegenden Leitungsmechanismus von Wasser in SPAF-303 zu erhalten. Es wurden

die drei Sulfonierungsgrade 30 %, 50 % und 80 % bei 33 % und 67 % RH mittels NMR-Spektroskopie vermessen. Bei diesen relativen Luftfeuchtigkeiten ist der Porenraum nicht vollständig gefüllt gegenüber der Luftfeuchtigkeit von 100 % RH und es ist anzunehmen, dass das sich ausbildende Confinement von den Proben bei 100 % RH unterscheidet. Um dies zu untersuchen wurde die neu entwickelte Analysemethode basierend auf der Kombination von Impedanz- und NMR-Spektroskopie bei Netzwerken mit paramagnetischen Zentren angewandt.

Die drei Netzwerke zeigten unabhängig von der relativen Luftfeuchtigkeit ebenfalls zwei Signale neben dem des Netzwerks (Abb. 14A und C). Hierbei konnte aufgrund des Verhältnisses der beiden Signale zu dem des Netzwerks nachgewiesen werden, dass es sich hierbei um das adsorbierte Wasser handelte. Mit steigender Temperatur sind nur noch zwei Signale detektierbar (Abb. 14B und D), wobei kein breites Wasser-Signal mehr vorhanden ist.

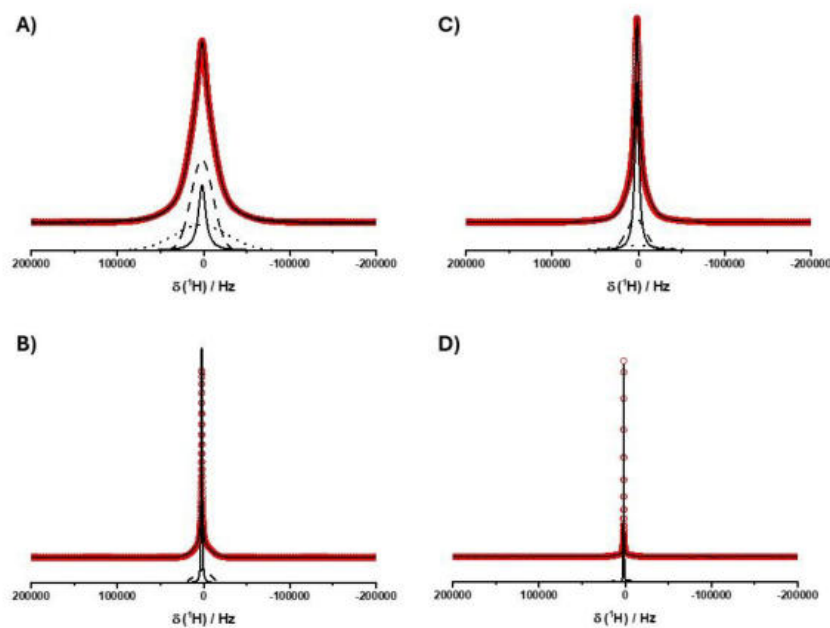


Abb. 14: ^1H single pulse (SP) NMR-Spektren von SPAF-303_{0.8} bei 33 % RH (A und B) und 67 % RH (C und D). Die Graphen A) und C) zeigen das Netzwerk bei ca. 220 K und B) und D) bei ca. 370 K. Unter den Spektren befinden sich die Einzelsignale, die mittels Fitting der Spektren erhalten wurde. Das gestrichelte Signal zeigt das Netzwerk, die gepunktete das immobilisierte Wasser mit einer FWHM von ca. 80 kHz und die kontinuierliche Linie das mobile Wasser mit kleiner 10 kHz FWHM. Die roten Kreise zeigen die addierte Intensität der einzelnen simulierten gefitteten Signale.

Die Wasser-Signale stehen in Abhängigkeit zueinander (Abb. 15), wobei das schmale Signal (Quadrat), das dem mobilen Wasser in der Pore zuzuordnen ist, mit zunehmender Temperatur zunimmt, wohingegen das breite Signal von ca. 70-80 kHz FWHM kontinuierlich abnimmt. Das breite Signal ist ebenfalls wieder dem Wasser, das sich in starker Wechselwirkung zur Porenwand befindet, zuzuordnen. Für beide Luftfeuchtigkeiten unterscheidet sich hierbei der Sulfonierungsgrad von 50 % zu den anderen in der Studie. So zeigt dieser Sulfonierungsgrad

die geringste Entropie von $55 \text{ J mol}^{-1} \text{ K}^{-1}$ für 33 % RH und $79 \text{ J mol}^{-1} \text{ K}^{-1}$ für 67 % RH, was einen Unterschied von mindestens $90 \text{ J mol}^{-1} \text{ K}^{-1}$ zu den anderen Sulfonierungsgraden entspricht. Die Enthalpie beträgt 11 kJ mol^{-1} (33 % RH) und 20 kJ mol^{-1} (67 % RH) und ist um mindestens 17 kJ mol^{-1} geringer. Dies kann ebenfalls der alternierenden Anordnung der Sulfonsäuregruppen im Netzwerk zugeordnet werden, wie es bereits bei der Analyse der Proben unter 100 % RH postuliert wurde, da sich hierbei die Entropien und Enthalpien nicht wesentlich von denen bei geringerer Luftfeuchtigkeiten unterscheiden.

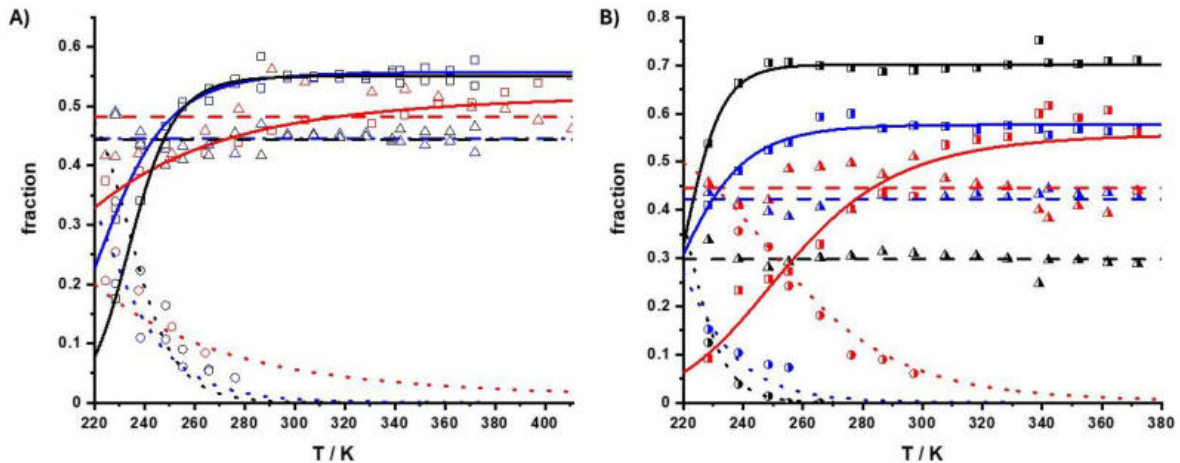


Abb. 15: Anteile der Resonanzen aus den ^1H SP NMR-Spektren von SPAF-303 mit einem Sulfonierungsgrad von 30 % (blau), 50 % (rot) und 80 % (schwarz) bei 33 % RH (A) und 67 % RH (B). Die Kreise zeigen den Anteil des breiten Signals (immobile Spezies), die Quadrate die der mobilen Spezies und die Dreiecke den Anteil des Netzwerks.

Bei den Spin-Gitter-Relaxation-Messungen zeigten alle Proben ein biexponentielles Verhalten. Aufgrund des Verhältnisses der beiden Komponenten zueinander, was das Verhältnis Wasser/Netzwerk wiedergibt, war ersichtlich, dass die beiden Wasserregime sich nicht in ihrer T_1 -Zeit unterscheiden. Alle untersuchten Confinements wiesen hierbei sehr kurze Relaxationszeiten von $100 \mu\text{s}$ bis hin zu einstelligen ms auf. Diese kurzen Relaxationszeiten bestätigten erneut, dass paramagnetische Zentren in den Netzwerken vorhanden waren, die aufgrund der metallkatalysierten Syntheseroute im Netzwerk verblieben sind. Hierbei besaß das Netzwerk mit 50 % Sulfonierungsgrad sowohl für 33 % als auch 67 % RH die kürzeste Relaxationszeit. Um die Korrelationszeiten zu ermitteln, wurde die BPP-Methode verwendet, die hierbei näherungsweise Anwendung findet. So konnten mittels der Korrelationszeiten die Diffusionskonstanten und daraus anhand der Nernst-Einstein-Beziehung die mikroskopische Leitfähigkeit ermittelt werden (Abb. 16A). Der Vergleich der mikroskopischen und makroskopischen Leitfähigkeit miteinander ergab, dass diese nicht übereinstimmten. Die mikroskopische Leitfähigkeit war 3 bis 5 Größenordnungen größer als die makroskopische Leitfähigkeit. Dies zeigte, dass in dem starken Confinement die Diffusion

der Wassermoleküle und Oxonium-Ionen nicht mehr frei erfolgen kann, sondern aufgrund der teilgefüllten Poren die Porenräume nicht mehr kontinuierlich miteinander verbunden sind, sondern Verjüngungen, sogenannte *Bottlenecks*, aufweisen.

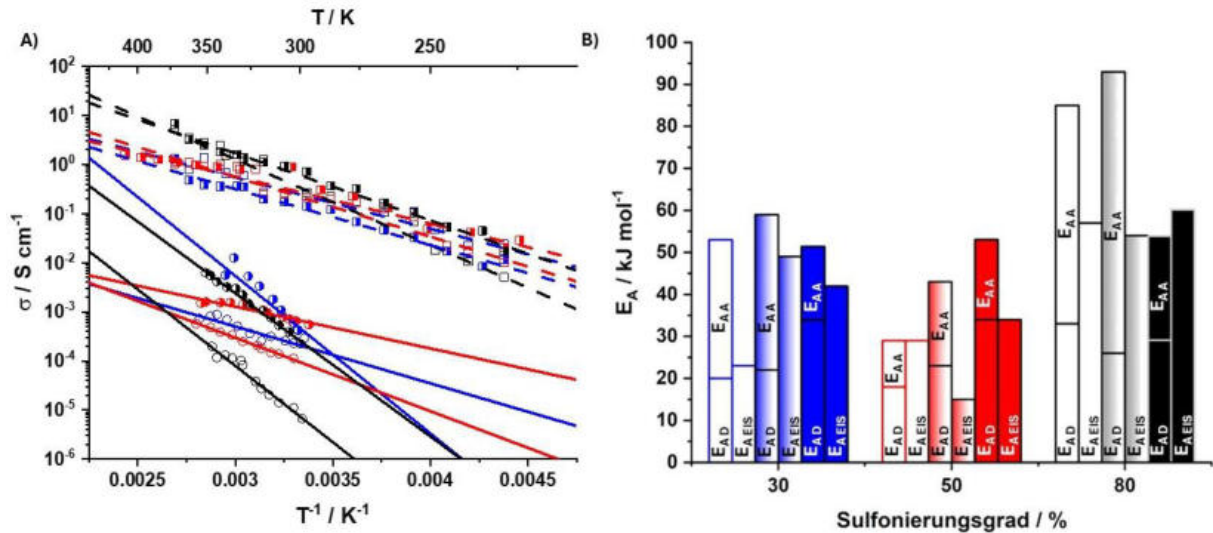


Abb. 16: A) Arrhenius-Auftragung der Leitfähigkeiten ermittelt anhand Impedanz- (Kreise) und NMR-Spektroskopie (Quadrate). σ_{NMR} wurde anhand der Diffusionskonstanten mit der Nernst-Einstein-Beziehung berechnet. Die Linien dienen als optisches Hilfsmittel. Leere Symbole sind bei 33 % RH und halb gefüllte bei 67 % RH. Der Farbcode beschreibt SPAF-303_{0,3} mit blau, SPAF-303_{0,5} mit rot und SPAF-303_{0,8} mit schwarz. B) Auftragung der Aktivierungsenergien ermittelt anhand von NMR-Spektroskopie (Diffusionsmessung E_{AD} und Austausch zwischen den beiden Wasserregimen E_{AA}) sowie der Aktivierungsenergie bestimmt durch Impedanz-Spektroskopie (E_{AEIS}). Der Farbcode folgt dem unter A). Leere Säulen entsprechen 33 % RH, halb gefüllte 67 % RH und ganz gefüllte 100 % RH.

Der Vergleich der ermittelten Leitfähigkeiten und die daraus bestimmten Aktivierungsenergien zeigte, dass bei 33 % RH die Aktivierungsenergie der makroskopischen Leitfähigkeit (E_{AEIS}) mit steigendem Ladungsträgergehalt zunahm (Abb. 16B). Die Sulfonierungsgrade 50 % und 80 % zeigten hierbei eine deutliche Abhängigkeit der makroskopischen Leitfähigkeit von der Diffusion und dem Austauschprozess zwischen den Wasser-Regimen, wohingegen SPAF-303_{0,3} hauptsächlich durch die Diffusion bestimmt wird. Bei 67 % RH ist SPAF-303_{0,5} hervorzuheben, da die mikroskopische Leitfähigkeit (E_{AD}) ein deutliches Minimum aufwies. Diese niedrige Aktivierungsenergie von 15 kJ mol^{-1} beruht unter anderem auf der alternierenden Anordnung der Sulfonsäuregruppen im Netzwerk. Die beiden Netzwerke SPAF-303_{0,3} und SPAF-303_{0,8} zeigten mehr als das Doppelte für E_{AEIS} . Neben der Aktivierungsenergie für die Diffusion ist hier der Austauschprozess maßgeblich mitentscheidend für den Leitungsmechanismus. Dies zeigte, dass der Einfluss des Wassergehalts der Probe einen maßgeblichen Einfluss auf die Leitfähigkeit besitzt, sodass die Diffusion ungehindert erfolgen kann und das Netzwerk diese nicht hindert. Zudem ist die alternierende Anordnung der Sulfonsäuregruppe unabhängig vom Wassergehalt der Probe zu favorisieren, da dies die Aktivierungsenergie entscheidend herabsetzt.

2.3. Thermodynamically Stable Functionalization of Microporous Aromatic Frameworks with Sulfonic Acid Groups by Inserting Methylene Spacers

Die Publikation stellt eine thematische Weiterentwicklung der von unserem Lehrstuhl publizierten Netzwerke dar. Die Netzwerke SPAF-1^[110] und SPAF-303^[102] zeichnen sich durch Sulfonsäuregruppen aus, die an einen Phenylring gebunden sind. Diese Bindung ist als reversible Bindung unter aziden Bedingungen und hohen Temperaturen bekannt. Aufgrund dessen wird diese ebenfalls als Schutzgruppe in der organischen Chemie verwendet. Dies limitiert das Einsatzgebiet der Materialien oder führt zu einer möglichen Degradation des Materials unter Abspaltung von Schwefelsäure. So war es Ziel ein nanoporöses Netzwerk mit kovalent gebundenen Sulfonsäuremethylen-Gruppen darzustellen. Die Einführung von Sulfonsäuremethylen-Gruppen soll eine irreversible Knüpfung der Sulfonsäuregruppen an das Netzwerk ermöglichen. Wie bereits in den vorangegangenen Arbeiten (Kapitel 2.1 und 2.2) gezeigt wurde, ist für eine herausragende Protonenleitung eine möglichst ungehinderte Diffusion im Netzwerk, Ausbildung eines starken Confinements für die Rückhaltekraft des Wassers in dem Netzwerk sowie eine mögliche Nanostrukturierung der Porenwand notwendig. Aufgrund dessen war es Ziel die Sulfonsäuregruppe mittels eines kleinen Moleküls an das Grundgerüst des nanoporösen Netzwerks postsynthetisch zu binden. Eine direkte Syntheseroute ist aufgrund der metallkatalysierten Syntheseroute des Netzwerks nicht möglich, da hierbei der Pd-Katalysator passiviert werden würde oder Nebenreaktionen auftreten würden.

Um das Netzwerk zu synthetisieren, wurde ausgehend von PAF-2 das Chloromethylen-PAF-303 (CIMPAF-303) mittels Blanc-Reaktion dargestellt (Abb. 17). Bei der Blanc-Reaktion wird eine Hydroxymethylen-Gruppe an den Phenylring addiert und anschließend mittel Salzsäure die Hydroxy-Gruppe gegen Chlor ausgetauscht. Diese Reaktion ermöglichte die Einführung einer kovalent gebundenen Methylen-Gruppe in das Netzwerk. Anschließend konnte in einer zweiten Stufe die funktionelle Gruppe gegen eine Sulfonsäuregruppe ausgetauscht werden, sodass das Sulfonsäuremethylen-PAF-303 (SMPAF-303) erhalten wurde.

Thermodynamically Stable Functionalization of Microporous Aromatic Frameworks with Sulfonic Acid Groups by Inserting Methylene Spacers

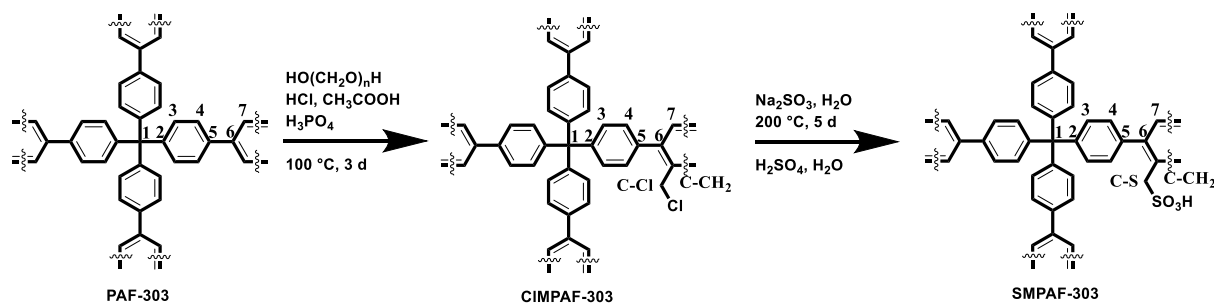


Abb. 17: Synthese des Netzwerks Sulfonsäuremethylen-PAF-303 (SMPAF-303) ausgehend von PAF-303 und der Zwischenstufe Chloromethylen-PAF-303 (ClMPAF-303). [Abbildung übernommen aus der Publikation^[111] nach der Lizenz CC BY 4.0]

Die erfolgreiche Darstellung der Zwischenstufe und der Ausbildung der kovalenten Bindung zwischen dem Aromaten und der Methylen-Gruppe konnte mittels Elementaranalyse, Ar-Physisorption, EDX-, IR-, NMR- und Röntgenphotoelektronenspektroskopie (engl.: *X-ray photoelectron spectroscopy (XPS)*) nachgewiesen werden. Die spektroskopischen Methoden wiesen dabei die Ausbildung der $\text{C}_{\text{ar}}\text{-CH}_2$ -Bindung sowie der $\text{CH}_2\text{-Cl}$ -Bindung nach. Zudem war es möglich den Chloromethylen-Anteil pro Wiederholungseinheit zu bestimmen, dieser betrug 1,2 Chloromethylen-Seitenarme pro Wiederholungseinheit und ist unter anderem dem Confinement von PAF geschuldet. Die nachfolgende Umsetzung zu SMPAF-303 wurde neben Elementaranalyse und spektroskopische Methoden mittels Titration bestätigt. Hierbei wurde eine Sulfonsäuremethylen-Seitengruppe pro Wiederholungseinheit nachgewiesen. Dies entspricht einem Sulfonierungsgrad von 17 %, im Vergleich zu SPAF-303. Während der zweistufigen Synthese zu SMPAF-303 nahm die innere BET-Oberfläche von $1317\text{ m}^2\text{ g}^{-1}$ (PAF-303) ab zu $743\text{ m}^2\text{ g}^{-1}$. Das Porenvolumen hat sich hierbei nahezu halbiert auf $0,337\text{ cc g}^{-1}$, wohingegen der Microporen-Anteil um 8 % auf 82 % angestiegen ist. Diese Ergebnisse bestätigten ebenfalls die erfolgreiche Einführung der Sulfonsäuremethylen-Seitengruppen. Zudem zeigten Wasser-Physisorption-Messungen (Abb. 18a), dass die Polarität von PAF-303 über ClMPAF-303 hin zu SMPAF-303 zunahm. Hierbei wies das sulfonierte poröse Netzwerk die höchste Polarität auf, sodass bis zu 400 cc g^{-1} gasförmiges Wasser adsorbieren konnten. Hierbei ist anzunehmen, dass mit einem höheren Sulfonierungsgrad mehr Wasser von dem Netzwerk adsorbiert werden könnte, ähnlich wie bei SPAF-303.

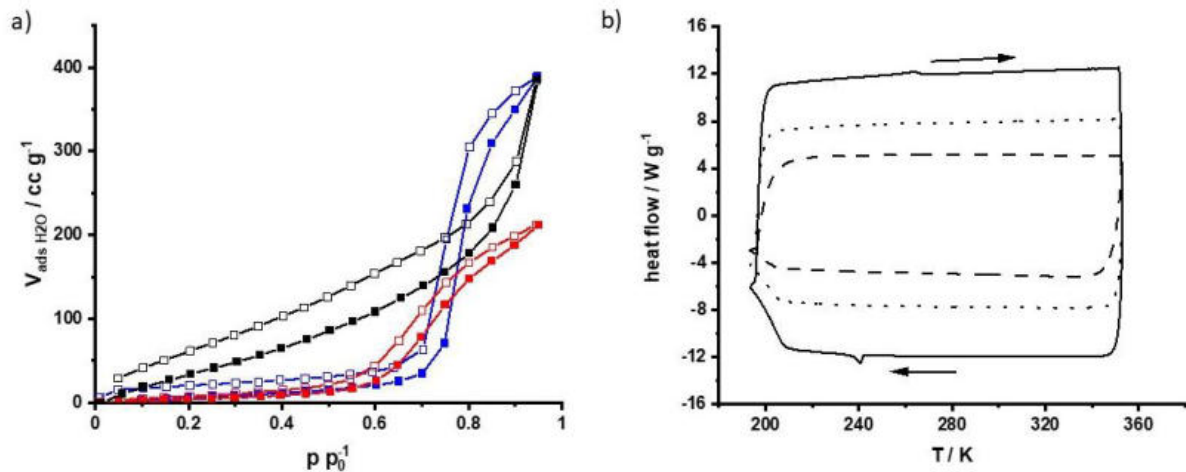


Abb. 18: H_2O -Physisorption-Messung von PAF-303 (rot), ClPAF-303 (blau) und SMPAF-303 (schwarz) bei 293 K. b) DSC-Messung von SMPAF-303 bei 100 % RH (kontinuierlich), 67 % RH (gepunktet) und 33 % RH (gestrichelt). [Abbildung nach der Lizenz CC BY 4 aus der Publikation^[111] übernommen]

Analog zum strukturell ähnlichen Netzwerks SPAF-303 zeigt SMPAF-303 bei der Adsorption von Wasser, dass 80 % des adsorbierten Wassers in Mikroporen adsorbiert wurden und ein starkes Confinement ausbilden, dies konnte anhand DSC-Messungen nachgewiesen werden (Abb. 18b). Bei den Luftfeuchtigkeiten von 33 % RH und 67 % RH war kein Bulk-Wasser ersichtlich. Bei diesen relativen Luftfeuchtigkeiten stehen alle Wasser-Moleküle in geringen Abstand zu den Porenwänden, insbesondere den in die Pore ragende Sulfonsäuregruppen, sodass starke Wechselwirkungen zwischen den Wasser-Molekülen und den Sulfonsäuregruppen ausgebildet werden konnten.

Die Leitfähigkeit der Protonen im Confinement wurde mittels Impedanzspektroskopie in Abhängigkeit der Luftfeuchtigkeit und Temperatur untersucht. Die erhaltenen Impedanz-Spektren in der Nyquist-Auftragung (Abb. 19a) zeigten drei Anteile der Probe (in der Pore, Korngrenzen und an der Grenzfläche zur Elektrode). Die Ermittlung der Anteile der Impedanz-Messung und die dazugehörigen Bestandteile der Probe und des Setups erfolgte analog der Methode wie im Kapitel 2.1 unter Abb. 12 beschrieben. Aus dem ersten Halbkreis, der die Leitung im Porenraum wiedergibt, wurde die Gleichstrom-Leitfähigkeit ermittelt und ergab eine Leitfähigkeit von bis zu $10^{-1} \text{ S cm}^{-1}$ bei 100 % RH (Abb. 19b) mit einer Aktivierungsenergie von ca. 38 kJ mol^{-1} .

Thermodynamically Stable Functionalization of Microporous Aromatic Frameworks with Sulfonic Acid Groups by Inserting Methylene Spacers

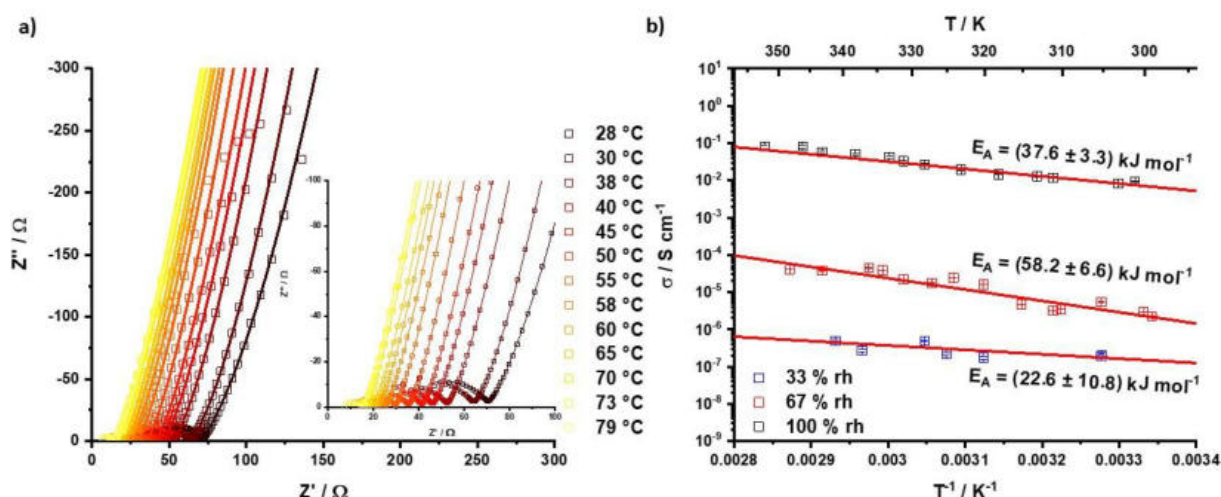


Abb. 19: a) Nyquist-Darstellung des SMPAF-303 mit 100 % RH. Die Vergrößerung zeigt den hochfrequenten Messbereich, der die Protonenleitung wiedergibt. b) Arrhenius-Aufragung der Leitfähigkeit von SMPAF-303 mit unterschiedlichen Luftfeuchtigkeiten. [Abbildung nach der Lizenz CC BY 4 aus der Publikation^[111] übernommen]

Diese hohe Leitfähigkeit, die sich in gleicher Größe wie bei Nafion und eine Magnitude unterhalb SPAF-303 befindet, weist ebenfalls eine ungehinderte Diffusion der Ladungsträger im Porenraum auf. Dies bestätigte die vorangegangene Hypothese, sehr kurze Seitenketten für die kovalente Anbindung der Sulfonsäuregruppen an das Netzwerk zu nutzen, sodass diese die Leitfähigkeit nicht merklich beeinflussen. Die Erkenntnisse dieser Arbeit zeigten die mögliche postsynthetische Modifikation des Netzwerks PAF-303 sowie den positiven Einfluss der offenporigen Struktur des Netzwerks für die Protonenleitung auf.

2.4. Ausblick

Die in dieser Arbeit vorgestellten Forschungsergebnisse lieferten einen detaillierteren Einblick in die Derivate des Netzwerks PAF-303 und die Anwendung als protonenleitendes Material. So hat sich gezeigt, dass der Porenraum, der durch seine drei Phenyrringe aufgespannt wird, ideal eignet ist, um postsynthetisch modifiziert zu werden. Hierbei hat sich gezeigt, dass die offene Porenstruktur eine homogene Verteilung der Sulfonsäuregruppen in SPAF-303 ermöglicht. Die homogene und alternierende Verteilung der Sulfonsäuregruppen in der adamantanartigen Struktur ermöglichten trotz des sehr starken Confinements eine herausragende Protonenleitung, wobei ein neuer Mechanismus der neben der Diffusion den Austausch zweier Wasserregime, stark gebundenem und mobilem Wasser in der Pore, mit einbezieht. Dieses Wissen in Verbindung mit der Variation der Synthesebedingungen galt es auf das Netzwerk SMPAF-303 anzuwenden, um die Stabilität der Sulfonsäuregruppen im Netzwerk zu erhöhen. Die erfolgreiche Darstellung von SMPAF-303 zeigte die Machbarkeit der Einbringung von Sulfonsäuremethylen-Seitenketten in das Netzwerk. Hierbei wurde ein Sulfonierungsgrad von 17 % erreicht. Es gilt diesen Sulfonierungsgrad durch weitere Optimierung der Synthesebedingungen und -parameter gezielt zu erhöhen. Hierfür muss ein Lösungsmittel-, Temperatur- und Reaktanten-Screening durchgeführt werden um einen höheren Halogenmethylierungsgrad der Vorstufe von SMPAF-303 zu erzielen. So soll es möglich sein, eine alternierende Struktur im Porenraum aus hydrophilen und hydrophoben Gruppen zu erlangen, dass sich Leitungskanäle im offenporigen Netzwerk bilden, die zu einer Reduzierung der Aktivierungsenergie führen, wie dies bei SPAF-303_{0,5} vorlag.

Als weiterer Schritt kann an solch einem Netzwerk der Mechanismus der Protonenleitfähigkeit untersucht werden. Hierzu kann die beschriebene Methode der Bestimmung der Spin-Gitter-Relaxationszeit verwendet werden, vorausgesetzt es sind in dem Netzwerk paramagnetische Zentren aufgrund der vorangegangenen Synthese vorhanden und diese Zentren ortsfest im Netzwerk verankert sind. Die vorgestellte Kombination aus NMR- und Impedanz-Spektroskopie ermöglicht ebenfalls, den Leitungsmechanismus in Materialien aufzuklären, die ein starkes Confinement in Anwesenheit von paramagnetischen Zentren aufweisen, wie es beispielweise bei metallorganischen-Gerüstverbindungen der Fall ist.

Als nachfolgender Schritt sollte der Einsatz unter realitätsnahen Bedingungen untersucht werden. Hierfür müssen Membranen basierend auf den Netzwerken hergestellt werden. Eine mögliche Grundlage könnte die Abscheidung des Materials aus einer Suspension des Netzwerks in einem Lösemittel auf dem porösen Elektrodenmaterial darstellen. Hierbei muss

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ein geeignetes Lösemittel ermittelt werden, das dem Quellverhalten des Netzwerks entgegenwirkt, um anschließende Spannungsrisse bei der Trocknung der Membran zu vermeiden. Mit der hergestellten Membran kann aufgrund der Nanoporosität des Netzwerks die Wasserevaporation unterbunden werden und die PEM-Brennstoffzelle bei höheren Temperaturen, ähnlich dem Arbeitsbereich von Phosphorsäure-Brennstoffzellen (150 °C), betrieben werden. Für diese Anwendungen gilt es die Gasseparationswirkung und Permeation zu untersuchen und die chemische und physikalische Langzeitstabilität festzustellen.

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4. Publikationen

Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework

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Simon F. Winterstein

- Projektplanung und Durchführung
- Synthese und Charakterisierung der Monomere und Netzwerke
- Durchführung der Analytik
- Auswertung und Interpretation des Gesamtdatensatzes
- Planung und Formulierung des Manuskripts

Alexei F. Privalov

- *static-field gradient* NMR-Messungen und Interpretation

Christopher Greve

- *wide-angle X-ray scattering* Messungen und Auswertung

Renée Siegel

- Festkörper-NMR Messungen

Björn Pötzschner

- Berechnung der Korrelationszeiten und Interpretation

Michael Bettermann

- *differential scanning calorimetry* Messungen
- *thermal gravimetric analysis* Messungen

Lea Adolph

- Postsynthetische Modifikation der Netzwerke

Jana Timm

- H₂O-Physisorption-Messungen

Roland Marschall

- Design des Manuskripts

Ernst A. Rößler

- Interpretation der Relaxation- und Korrelationsdaten

Eva M. Herzig

- Auswertung und Interpretation der *wide-angle X-ray scattering* Messungen

Michael Vogel

- Design des Manuskripts
- Auswertung und Interpretation der NMR-Diffusionsdaten

Jürgen Senker

- Interpretation der Relaxation- und Korrelationsdaten
- Projektplanung und Supervision
- Planung und Aufsetzen des Manuskripts

Understanding of Proton Conduction in Confinement of SPAF-303

Das Manuskript wurde am Lehrstuhl Anorganische Chemie III der Universität Bayreuth sowie dem Nordbayrischen NMR-Zentrum durchgeführt. Die Beiträge der Arbeit sind wie folgt:

Simon F. Winterstein

- Projektplanung und Durchführung
- Durchführung der Messungen
- Auswertung des Gesamtdatensatzes
- Planung und Aufsetzen des Manuskripts

Renée Siegel

- Durchführung der Messungen

Jürgen Senker

- Auswertung und Interpretation der Datensätze
- Projektplanung und Supervision
- Planung und Aufsetzen des Manuskripts

Thermodynamically Stable Functionalization of Microporous Aromatic Frameworks with Sulfonic Acid Groups by Inserting Methylene Spacers

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Simon F. Winterstein

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- Auswertung und Interpretation des Gesamtdatensatzes
- Planung und Formulierung des Manuskripts

Michael Bettermann

- Synthese der Monomere und Netzwerke
- Charakterisierung der Verbindungen

Jana Timm

- H₂O-Physisorption-Messungen

Roland Marschall

- Design des Manuskripts
- Supervision

Jürgen Senker

- Projektplanung und Supervision
- Planung und Aufsetzen des Manuskripts

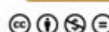
4.1. Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework



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Article

Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework

Simon F. Winterstein, Alexei F. Privalov, Christopher Greve, Renée Siegel, Björn Pötzschner,[†] Michael Bettermann, Lea Adolph, Jana Timm, Roland Marschall, Ernst A. Rössler, Eva M. Herzig, Michael Vogel, and Jürgen Senker*



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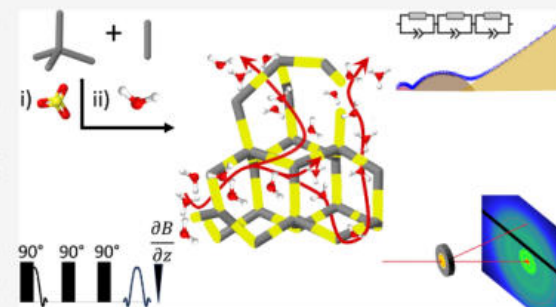
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ABSTRACT: Sulfonated, cross-linked porous polymers are promising frameworks for aqueous high-performance electrolyte-host systems for electrochemical energy storage and conversion. The systems offer high proton conductivities, excellent chemical and mechanical stabilities, and straightforward water management. However, little is known about mass transport mechanisms in such nanostructured hosts. We report on the synthesis and postsynthetic sulfonation of an aromatic framework (SPAF-2) with a 3D-interconnected nanoporosity and varying sulfonation degrees. Water adsorption produces the system SPAF-2^{H₂O}. It features proton exchange capacities up to 6 mequiv g^{−1} and exceptional proton conductivities of about 1 S cm^{−1}. Two contributions are essential for the highly efficient transport. First, the nanometer-sized pores link the charge transport to the diffusion of adsorbed water molecules, which is almost as fast as bulk water. Second, continuous exchange between interface-bound and mobile species enhances the conductivities at elevated temperatures. SPAF-2^{H₂O} showcases how to tailor nanostructured electrolyte-host systems with liquid-like conductivities.



INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) are promising devices for the sustainable conversion of chemically stored energy into electricity.¹ The active component of a PEMFC is the membrane-electrode assembly (MEA).² It consists of electrically conductive carbon black that is coated with platinum nanoparticles serving as catalysts for the oxidation of hydrogen and the reduction of oxygen on either side of the MEA.¹ The sandwiched proton-conducting membrane shuttles protons from the anode to the cathode, utilizing charge compensation and the water formation at the cathode. The membrane avoids the mixing of hydrogen and oxygen and minimizes electronic leakage currents.³

The state-of-the-art material for proton conductive polymer electrolyte membranes is Nafion.⁴ It is a branched fluorinated copolymer with sulfonic acid groups at the side chain ends.^{5,6} It features high ion exchange capacities (IECs) of about 1 mequiv g^{−1} and excellent proton conductivities up to 10^{−1} S cm^{−1} at 353 K and 100% relative humidity (RH).^{6,7} As adsorbed water is attracted to the sulfonated side chains, water-rich channels are formed causing microphase separation.^{5,8} The fluorinated, hydrophobic part provides the mechanical stability of the swollen membrane and serves as a confinement for the embedded water molecules and oxonium ions. The channels typically span several nanometers leading to moderate

confinement effects on the dynamics and the transport properties of H₂O/H₃O⁺.^{5,9–13}

Low hydration levels favor vehicle transport, which facilitates charge transport by diffusion of oxonium ions.^{9,14–16} Higher hydration degrees favor the Grotthuss mechanism,^{16–18} also referred to as the hopping or relay mechanism. Here, charge transport is mediated via protons that are transferred from water to water molecules.^{19,20} This requires structural reorientation and displacement of water molecules to transfer protons from one water molecule to another. The transformation involves the formation of two clusters, the Zundel (H₅O₂⁺) and the Eigen (H₉O₄⁺) ions.^{9,21,22} For systems with high proton densities it was suggested¹⁹ that it is sufficient for the water molecules to perform small reorientations to enable the transfer of protons between oxonium ions and acid groups (pseudoshuttling).²⁰

Nafion's water channels influence the transport mechanisms. The confinement, although moderate, creates a slightly higher

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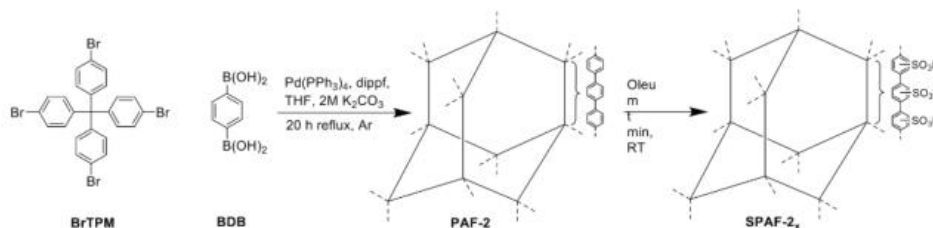
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Scheme 1. Synthesis of Tetrakis(4-bromophenyl)methane (BrTBPM) and Diboronic Acid (BDB) to PAF-2 and Subsequent Sulfonation to Sulfonated PAF-2 with a Sulfonation Degree x (SPAF-2 _{x})



translational order for adsorbed molecules¹² and distorts the hydrogen bond network¹³ typical for bulk water and distributes the motional modes¹¹ of the water molecules and oxonium ions. These dynamic heterogeneities include water molecules and oxonium ions strongly attracted to the sulfonic acid groups and free water in the inner part of the channels. While the former molecules are slowed down and restricted in their mobility, the latter ones diffuse freely in the channel interior.

Still, Nafion suffers from a limited working temperature up to 353 K as water is only weakly attached to the framework. This makes complicated water management necessary to avoid dissolution effects leading to a mechanical failure of the membranes.^{5–8,23} Additionally, Nafions synthesis is expensive, and environmentally harmful products are formed during its long-term degradation.^{6,24,25} This and the increasing demands for higher working temperatures and proton conductivities inspired the development of a variety of inorganic, organic, and hybrid materials that combine high proton conductivities with stronger retention forces for the water molecules. Promising material classes are polyoxometalates (POMs),²⁶ functionalized silicas,²⁷ metal–organic frameworks (MOFs),^{26,28–30} porous organic frameworks (POFs),^{31,32} covalent–organic frameworks (COFs),^{26,33} and block copolymers.³⁴

All of these materials have in common that they are micro- and/or mesoporous and feature an interconnecting pore structure. The strong host–guest interactions, typical for such systems, lead to higher water adsorption enthalpies, rendering the adsorbate molecules less likely to be desorbed at elevated temperatures. Table S1 shows that MOFs and COFs reach proton conductivities comparable to Nafion. Nevertheless, these systems often lead to powders composed of small particles.^{17,26,35–40} This complicates the manufacturing of mechanically robust and gastight membranes. Mixed matrix membranes combine the mechanical stability of polymer membranes with the favorable properties of the porous particles.^{5,17,23,41,42} The porous additives serve as reservoirs for both water and protons in turn easing the strong dependence of the proton conductivity on the hydration level and temperature pure Nafion membranes exhibit.

The small nanometer-sized cavities, typical for these materials, lead to strong confinement effects for the rotational and translational water dynamics.^{43–47} If attractive forces prevail between the water molecules and the host surfaces, prominent effects are a slowdown of molecules close to the inner surfaces, leading to dynamic heterogeneities, and a reduction of the self-diffusion constants up to 3 orders of magnitude compared to bulk water.^{43–45} If repulsive host–guest interactions or quantum-friction effects dominate, ultrafast water self-diffusion was reported in nanochannels.^{46,47}

Up to now, mechanistic studies were carried out only for a few systems, and a general understanding of the underlying processes is missing. The chemical surface structure and related host–guest interactions become vitally important to establish efficient proton conduction paths.^{34,48–51} High proton conductivities were observed when the functional surface groups were close enough to each other to shuttle protons^{49,51} or allow for positioning of water molecules to form continuous hydrogen bond networks.^{48,50,51} In both cases trains are induced along which protons are then transported without long-range mass transport as for Grotthuss-type mechanisms and pseudoshuttling.^{19,20}

Here, we present a comprehensive study, investigating the synthesis, properties, and proton conductivities of aqueous electrolyte–host systems based on the sulfonated porous aromatic framework PAF-2.^{35,52,53} Although PAFs are amorphous, they are often described in an idealized way by sp^3 carbon atoms positioned on a diamond-type lattice following the reticular synthesis concept.^{32,54,55} These central units are connected along the four covalent bonds of the sp^3 carbon atoms by linkers consisting of linear chains of three (PAF-2) and two (PAF-1) benzene rings bonded via the 1,4-positions. Due to kinetic control, defects like one-sided linker termination and partial framework interpenetration are built into the frameworks, preventing long-range order. This leads to highly porous, amorphous materials with nanometer-sized 3D-interconnected adamantane-like pores.

The synthesis route allows for preparing sulfonated frameworks with high and varying sulfonation degrees (SPAF-2 _{x}) without compromising the framework integrity. By combining electrochemical impedance spectroscopy (EIS), nuclear magnetic resonance (NMR) spectroscopy, and static-field gradient (SFG) NMR experiments, we investigated how the proton conductivity, the local mobility, and self-diffusion of H_2O/H_3O^+ are linked in nanoscale confinements that change as a function of the framework hydrophobicity, RH, and temperature. We provide intriguing insights into why sulfonated PAFs allow for liquid-like proton conductivities of up to 1 S cm^{-1} , in spite of the strong confinement, extending the suite of reported conduction mechanisms.

RESULTS AND DISCUSSION

Host System: SPAF-2 _{x} . PAF-2 was synthesized following a protocol published by Kaskel and co-workers using tetrakis(triphenylphosphine)palladium(0) and diisopropylphosphineferrocene (dippf) as catalysts.⁵² For gas-phase sulfonation, PAF-2 was exposed to an SO_3 atmosphere for 30, 90, and 180 s (Scheme 1).³⁵ The resulting products SPAF-2 _{x} , where x denotes the sulfonation degree, were washed to remove nonbonded SO_3 molecules. We characterized all frameworks

by infrared (IR) and ^{13}C NMR spectroscopies, elemental analysis (EA), energy-dispersive X-ray spectroscopy (EDX), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), Ar and H_2O physisorption, X-ray powder diffraction, and titration (Figures S1–S5 and Tables S2–S8). The resulting stoichiometries are given in Table 1.

Table 1. Average Stoichiometries and Sulfonation Degree x of PAF-2 and SPAF-2 $_x$ from EA, EDX, and Titration^a

sample	stoichiometry	$x = y/6$
PAF-2	$\text{C}_{37}\text{H}_{24}\text{Br}_{0.1}$	
SPAF-2 $_{0.3}$	$\text{C}_{37}\text{H}_{22.2}(\text{SO}_3\text{H})_{1.8}\text{Br}_{0.1} \cdot 0.5 \text{H}_2\text{O}$	0.30
SPAF-2 $_{0.5}$	$\text{C}_{37}\text{H}_{21.1}(\text{SO}_3\text{H})_{2.9}\text{Br}_{0.2} \cdot 7.5 \text{H}_2\text{O}$	0.48
SPAF-2 $_{0.8}$	$\text{C}_{37}\text{H}_{19.3}(\text{SO}_3\text{H})_{4.8}\text{Br}_{0.2} \cdot 4.5 \text{H}_2\text{O}$	0.80

^aAdded water molecules are adsorbed in the framework. Additionally, small proportions of Pd (0.02 at %) and Fe (0.08 at %) were found. On average, they amount to 0.008 Pd and 0.03 Fe atoms to be added to the molecular formulas. For calculating the sulfonation degree $x = y/6$ the stoichiometries were rewritten as $\text{C}_{37}\text{H}_y(\text{SO}_3\text{H})_z\text{Br}_w \cdot w \text{H}_2\text{O}$. Details of the evaluation are given in Tables S3–S7.

High cross-linking degrees of about 90% were determined for PAF-2. The remaining unconnected benzene rings are terminated with Br and small proportions of about 0.02 atom % palladium and 0.08 atom % iron were additionally detected. They are residuals of the used catalysts of the cross-coupling reaction and will occur most likely in an oxidized form as paramagnetic Pd^{2+} and Fe^{3+} . These impurities could not be removed by subsequent sulfonation and Soxhlet extraction, suggesting immobilization within the framework. The analyses show that the framework and residual Br end groups remain intact upon sulfonation and that the sulfonic acid groups are covalently attached to the framework's phenyl rings. The corresponding ^{13}C NMR resonances (Figure S1A) broaden markedly indicating that the $-\text{SO}_3\text{H}$ units are distributed over the 12 possible aromatic carbon atoms (C–H positions) of the three benzene rings of one rack. Together with the rotational freedom of the benzene rings, on average the SO_3H groups distribute over the inner pore surfaces.

The sulfonation degree $x = y/6$ (Table 1) for the three derivatives amounts to roughly 30, 50, and 80%. This corresponds to an average sulfonation of two, three, and five of the six phenyl rings of the repeating unit, for the likely case that only monosulfonation of the phenyl rings occurs. Moreover, IECs of 2.77 mequiv g^{-1} (SPAF-2 $_{0.3}$), 4.12 mequiv g^{-1} (SPAF-2 $_{0.5}$), and 5.67 mequiv g^{-1} (SPAF-2 $_{0.8}$) were derived, which exceed the IEC of Nafion by up to six times.³⁸ The accessible amount of SO_3H units calculated from the IECs matches the stoichiometries, demonstrating that all sulfonic acid groups point into the pores and are accessible to adsorbed water molecules. Thus, all sulfonic acid groups will contribute to the proton conductivity of SPAF-2 derivatives

(see below). Neither the structural integrity nor the sulfonation degree changed during the temperature-dependent EIS and NMR spectroscopic measurements demonstrating the long-term stability of the sulfonated frameworks. This was shown by repeated ^{13}C NMR and IR spectroscopic (Figure S1A,D), and titration experiments (Figure S3 and Table S7).

Decomposition of SPAF-2 $_x$ ($x = 0.3, 0.5, 0.8$) sets in above 485 K (Figure S1C). At this temperature, the frameworks start to lose the attached sulfonic acid groups, as shown by coupled thermogravimetric analysis and mass spectrometry (TGA-MS) experiments (Figure S4). As such, all SPAF-2 $_x$ derivatives should be stable even under harsh conditions in high-temperature PEMFC that work around 450 K.

As previously reported, PAF-2 exhibits a remarkable micro- and mesoporosity with highly interconnected pore spaces (Figures S1B and S2).^{52,56} The Brunauer–Emmett–Teller (BET) surface area (Ar) and total pore volume amount to 1690 $\text{m}^2 \text{g}^{-1}$ and 1.20 $\text{cm}^3 \text{g}^{-1}$ (Table 2). About 50% of the total pore volume results from micropores with a maximum pore width of roughly 1 nm. The surface area and pore volume are roughly 20% larger than previously reported.^{52,57} We attribute this to a higher cross-linking degree. The hysteresis for the desorption branch of the isotherm suggests a moderate capability to swell, which is probably caused by the remaining unconnected end groups allowing for a certain flexibility.⁵² Furthermore, the magnitudes of the observed surface areas, pore volumes, and narrow pore size distributions suggest partial framework interpenetration.^{54,55} Sulfonation causes severe decreases in both surface area and pore volume. For SPAF-2 $_{0.3}$ roughly 20% of the original pore volume remains accessible to Ar, while it is further reduced to about 10% for SPAF-2 $_{0.8}$. This is accompanied by a decrease in the micropore fraction, indicating that preferentially micropores contract upon sulfonation due to the strong increase in multipole interactions between neighboring SO_3H units.

Due to kinetic control for PAF-2 synthesis, all frameworks are amorphous (Figure S1E).^{32,54,55} Their X-ray powder patterns share broad maxima at 17°, 23°, and 43° in 2 θ , suggesting that characteristic framework distances and topology do not change upon sulfonation. The observed intensity modulations are most likely caused by attaching sulfonic acid groups to the benzene rings. These results align with the ^{13}C MAS and IR spectroscopic analyses (Figure S1). Previous studies propose that the flexibility introduced by the remaining dangling bonds favors framework deformation and partial interpenetration, preventing the formation of long-range order. Nevertheless, locally, the frameworks will consist of connected adamantane-type units.

Electrolyte-Host System: SPAF-2 $^{\text{RH}}$. The water isotherm of PAF-2 (Figure 1A) shows the expected behavior (type V according to IUPAC classification)⁵⁶ of a hydrophobic framework. The water gate-opening partial pressure occurs at

Table 2. Ar Surface Areas, Total Pore Volume, and Micropore Ratio of PAF-2 and SPAF-2 $_x$

sample	BET SA(Ar) / $\text{m}^2 \text{g}^{-1a}$	DFT SA(Ar)/ $\text{m}^2 \text{g}^{-1b}$	pore volume/ cc g^{-1b}	micropore ratio/% ^b
PAF-2	1692	1761	1.263	48
SPAF-2 $_{0.3}$	352	380	0.271	46
SPAF-2 $_{0.5}$	136	153	0.25	17
SPAF-2 $_{0.8}$	124	123	0.198	19

^aCalculated using the BET equation. ^bDerived using an equilibrium model for a quenched solid density functional theory (QSDFT) slit-pore kernel (Ar at 87 K on carbon).

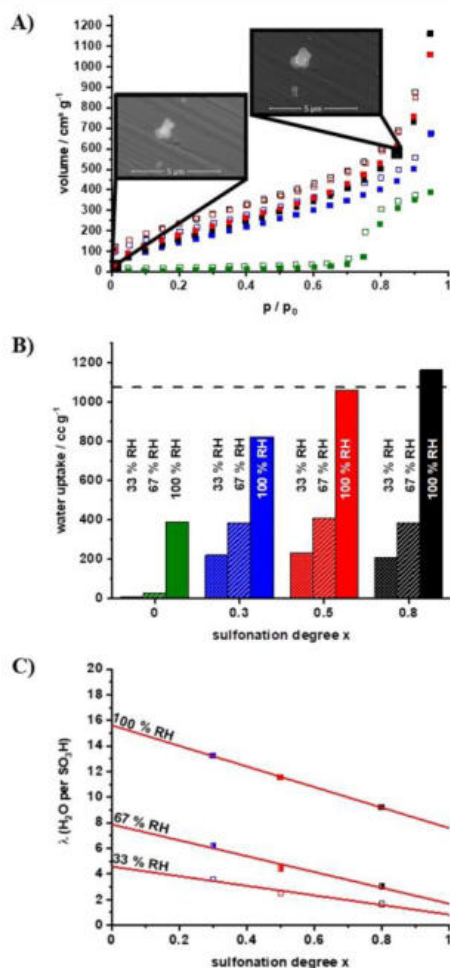


Figure 1. Water adsorbed in PAF-2 (green) and SPAF-2_x ($x = 0.3$ (blue), 0.5 (red), and 0.8 (black)). (A) H₂O isotherms measured at 293 K for PAF-2 and SPAF-2_x. SEM images obtained for SPAF-2_x at 1.3% RH and 89.9% RH are included as insets. (B) Water uptake at 33% RH (dotted), 67% RH (shaded), and 100% RH (full) derived from the water isotherms. The horizontal dashed line indicates when the original pore volume of PAF-2 would be filled with H₂O molecules. The volume is derived from the Ar uptake of PAF-2 assuming that H₂O and Ar follow the ideal gas equation (Figure S1B). (C) Number of water molecules per SO₃H group (λ) determined from the water isotherms at 33, 67, and 100% RH.

a RH of 70%. Below this value, water is repelled but adsorbs readily at higher RH. At 100% RH, PAF-2 takes up roughly 390 cm³ g⁻¹. Sulfonation makes the materials remarkably hydrophilic (Figure 1B). For SPAF-2_x, the water adsorption starts at low RH and continuously increases to values of 820 cm³ g⁻¹ ($x = 0.3$), 1060 cm³ g⁻¹ ($x = 0.5$), and 1160 cm³ g⁻¹ ($x = 0.8$) at 100% RH. This corresponds to an enhancement of the water uptake by 2 and 3 for 100% RH. However, the enhancement factors are on the order of a few hundred below the gate-opening RH of PAF-2.

In the latter regime, the water uptake depends markedly on the RH but is hardly affected by the sulfonation degree (Figure 1B). We attribute this to the strong retention forces caused by

the attractive interactions between the deprotonated sulfonic acid groups and the H₃O⁺ ions. In contrast, the framework retention caused by the SO₃H groups is overcome for high RH, rendering the framework contraction (Table 2) reversible. The contracted pores reopen, regenerating the originally accessible pore volume (Figure 1B). Thus, the adsorbed H₂O molecules and H₃O⁺ ions move more freely in the pore system. For 100% RH, the water uptake saturates for $x > 0.5$. This is accompanied by an increase of the particle sizes of about 10% as observed in environmental scanning electron microscopy (Figure 1A). In turn, the pore sizes and alignment of the framework racks are influenced by the water uptake.

DSC measurements for SPAF-2_x (Figure S5) reveal freezing and melting peaks during the cooling–heating cycle for 100% RH. The onset temperature of about 245 K (heating branch) is typical of ice melting in mesopores with average diameters smaller than 5 nm.⁵⁸ Based on the total water uptake (Figure 1B) and the molar melting enthalpy of ice⁵⁹ the freezable water fraction amounts to less than 15%. As the melting enthalpy might be changed in confined spaces, we regard the obtained freezable water fraction as the upper boundary. For 33 and 67%, no freezing and melting peaks were observed. Thus, in all cases, >85% of the water is adsorbed in confinements where water does not freeze and thus remains mobile for temperatures well below 273 K. This is promising for low-temperature applications. Transient water clusters and hydrogen bond networks typical for bulk water will be suppressed or distorted, rendering the formation of Zundel and Eigen ions needed for a Grotthuss-type proton transport unlikely. By contrast, the water in the larger channels of Nafion is susceptible to crystallization.^{5,60}

Considering that the water molecules are stored in micropores and subordinated in small mesopores, it is plausible that the water uptake is limited. We observed saturation for 100% RH and high sulfonation degree x (Figure 1B). Intriguingly, an equivalence of the molar volumes for water molecules adsorbed in SPAF-2_x and Ar in PAF-2 was found, which suggests that the pore volume of PAF-2 is retrieved upon water adsorption. As the maximum amount of water is limited, increasing x leads to higher H₃O⁺ concentrations. The number of water molecules per SO₃H group λ (Figure 1C) decreases linearly as a function of x . Roughly 13 water molecules are matched with one –SO₃H group for $x = 0.3$ and λ reduces to about 9 water molecules for $x = 0.8$, given that both samples are saturated at 100% RH. Lowering RH led to significantly lower λ values down to $\lambda = 2$, while preserving the general trend. The opposite behavior (increasing λ with rising x) was observed for materials like Nafion 117 and SPAF-1,^{35,61} where the water uptake is driven by solvation of the SO₃[–] and H₃O⁺ ions and not by the free adsorption volume available to the water molecules. At 100% RH λ of Nafion 117 and SPAF-2_{0.3}¹⁰⁰ are similar.⁶¹

SPAF-2_x^{RH} show some important characteristics. They take up roughly their own weight in water (e.g., 48 wt % of water for SPAF-2_{0.8}¹⁰⁰) without losing the framework integrity or changing phase and shape, which is advantageous compared to common exchange membranes.⁶² Due to the large IECs (up to 5.7 mequiv g⁻¹), a fluid with a high proton concentration is created in 3D pores, which promises high proton conductivities for SPAF-2_x^{RH} derivatives. As the water molecules are mainly confined to the microporous spaces, they exhibit strong host–guest interactions and are less likely to be desorbed

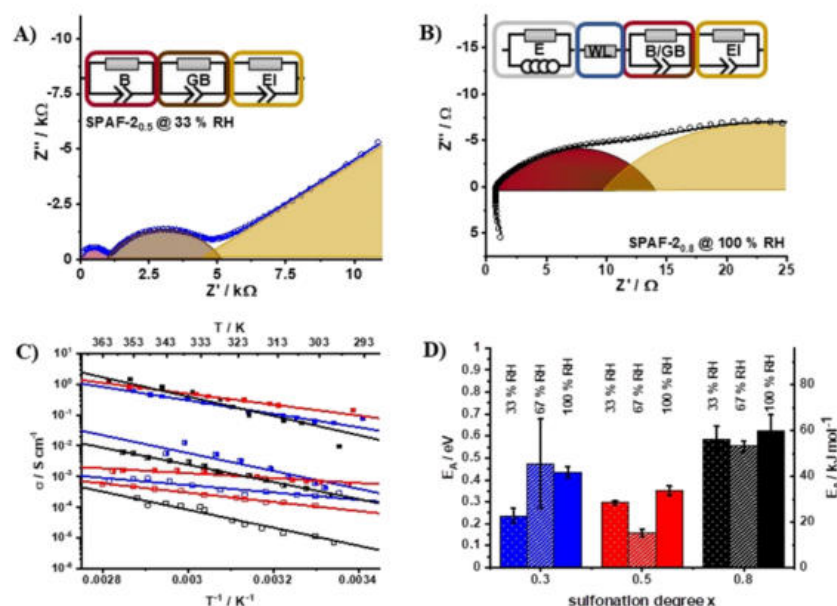


Figure 2. EIS measurements, conductivities, and activation barriers of SPAF-2_x^{RH}. (A) Nyquist plot of SPAF-2_{0.5}³³ at 303 K with an equivalent circuit containing RC elements for bulk in dark red (B), grain boundaries in brown (GB), and electrode interface in yellow (EI). (B) Nyquist plot of SPAF-2_{0.8}¹⁰⁰ at 306 K with the equivalent circuit consisting of elements for electrodes and cables in gray (E), a water film in blue (WL), bulk and grain boundaries in dark red/brown (B/GB), and an electrode interface in yellow (EI). (C) Arrhenius plot of σ for SPAF-2_{0.3} (blue), SPAF-2_{0.5} (red), and SPAF-2_{0.8} (black) for various relative humidities. Empty, half-filled, and filled symbols correspond to 33, 67, and 100% RH, respectively. While σ for 33 and 67% RH are bulk conductivities, the ones for 100% RH are joint bulk and grain boundary conductivities (Tables S10–S21). (D) Activation barriers for various sulfonation degrees and relative humidities.

compared to Nafion. As such, SPAF-2_x^{RH} offer less demanding water management for polymer fuel cell applications.

Proton Conductivity of SPAF-2_x^{RH}. EIS on pellets pressed from SPAF-2_x^{RH} powders revealed two main regimes. SPAF-2_{0.3}^{RH} and SPAF-2_{0.5}^{RH} equilibrated at 33 and 67% RH exhibited three half-circles in the Nyquist plots (Figures 2A, S9, S10, S13, and S14), which were well described by three RC elements in series. The capacities of the three RC elements in the equivalent circuit are characteristic for (i) bulk conduction ($C < 10^{-12}$ F), (ii) transport over the grain boundaries ($C < 10^{-7}$ F), and (iii) polarization and chemical reactions at the electrodes ($C > 10^{-4}$ F). As H⁺/H₃O⁺ are the only mobile charge carriers, we attribute the first two elements to the conduction of protons in the pore system of the individual SPAF-2_x^{RH} particles and the transport between the particles. The corresponding resistances R serve as a measure for DC conductivities σ_B and σ_{GB} .

The proton bulk conductivities σ_B in this regime reach values between 10^{-5} and 10^{-2} S cm⁻¹ (Figure 2C) and exhibit an Arrhenius temperature dependence. Proton conduction over the grain boundaries σ_{GB} is on average 2 orders of magnitude lower (Tables S10, S11, S14, and S15). Retarded proton transport between particles implies that the water molecules and oxonium ions are effectively confined to the SPAF-2_x^{RH} particles. The RH has a strong influence on the σ_B (Figure 2C). Equilibrating the samples at 67% instead of 33% RH enhances σ_B by up to 2 orders of magnitude. We attribute this to the larger number of water molecules per SO₃H unit (Figure 1C). The additional water improves the oxonium ion solvation, separates H₃O⁺/SO₃⁻ ion pairs more efficiently, and thus allows part of the framework porosity to be restored. In

turn, the mobility of the water molecules and oxonium ions increases.

In contrast, changing the sulfonation degree from 0.3 to 0.5 has only minor effects on σ_B (Figure 2C). This is unexpected, as the IEC almost doubles. Due to the strong confinement, the water uptake is limited by strong retention forces of the ion pairs, trapping H₃O⁺ ions within the vicinity of the sulfonic acid groups. Increasing the temperature from RT to 353 K improves σ_B by roughly 1 order of magnitude. The activation barriers (E_A) for the thermally activated conduction are similar (Figure 2D) and vary between 30 and 40 kJ mol⁻¹. H⁺ transport with E_A in this regime is typically considered as borderline between Grotthuss and vehicle mechanisms.^{19,63,64}

The impedance spectra for SPAF-2_{0.8}¹⁰⁰, SPAF-2_{0.5}¹⁰⁰, and SPAF-2_{0.3}¹⁰⁰ change markedly (Figures S11, S15, S17–S19). As the overall resistance is quite low in this regime, an equivalence circuit for the electrode was added to the refinements (Figure 2B). More importantly, the equivalence circuits for the bulk and the grain boundaries merge into one circuit as only one relaxation process is resolved in the distribution of relaxation times (Figure S6B) in addition to the electrode and electrode interface elements. This suggests that the protons and oxonium ions exchange freely between the pore volumes of the SPAF-2_x^{RH} particles and the grain boundary regions. This is intriguing, as it suggests that SPAF-2_x^{RH} derivatives, in particular when saturated at 100% RH, might be used as fuel cell separators without the need to prepare a homogeneous film as long as the hydrogen and oxygen gas permeabilities are low enough for the dense particle films. In particular, as the SPAF-2_x^{RH} electrolyte-host systems are long-term stable, shown by the EIS measurements repeated after several months.

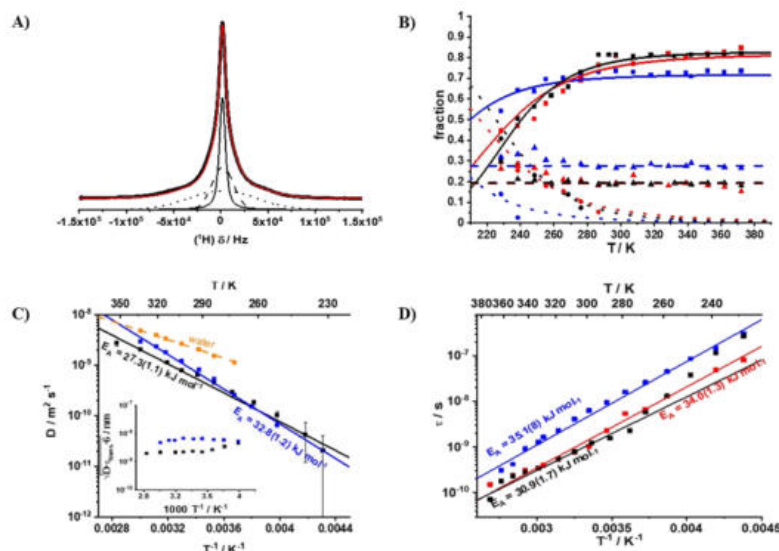


Figure 3. NMR spectroscopic studies of SPAF-2_x. (A) ¹H NMR spectrum of SPAF-2_{0.8}¹⁰⁰ at 224 K (black dots). The spectrum was fitted (red solid line) superimposing three signals representing mobile water (black solid line, fwhm < 10 kHz), framework (black dashed line, fwhm ≈ 27 kHz), and bound water (black pointed line, fwhm ≈ 81 kHz). (B) Proportion of protons of the mobile (squares, solid line) and immobile (circles, pointed line) H₂O/H₃O⁺ and of the framework (triangles, dashed lines) derived from the line shape analyses of the ¹H NMR spectra of SPAF-2_{0.3}¹⁰⁰ (blue), SPAF-2_{0.5}¹⁰⁰ (red), and SPAF-2_{0.8}¹⁰⁰ (black) (Figures S22–S24 and Table S22). The solid and pointed lines are refinements of eq 1. (C) Self-diffusion coefficients *D* from SFG NMR experiments for SPAF-2_x¹⁰⁰ [*x* = 0.3 (blue), 0.5 (red), 0.8 (black)] and liquid water (orange).⁶⁶ The inset of panel (C) shows the square root of 6*Dτ*_{trans} for SPAF-2_{0.3}¹⁰⁰ (blue) and SPAF-2_{0.8}¹⁰⁰ (black). (D) Correlation times *τ*_{trans} for the H₂O/H₃O⁺ translation calculated from *T*₁ measurements of SPAF-2_x¹⁰⁰ [*x* = 0.3 (blue), 0.5 (red), and 0.8 (black)].

For a RH of 100%, $\sigma_{B/Gb}$ rises by roughly 2 orders of magnitude with only a moderate dependence of $\sigma_{B/Gb}$ on the sulfonation degree. At about 353 K, $\sigma_{B/Gb}$ varies between 1.4 S cm⁻¹ for SPAF-2_{0.8}¹⁰⁰ and 0.6 S cm⁻¹ for SPAF-2_{0.3}¹⁰⁰ (Tables S12, S16 and S20). These conductivities are about four decades higher compared to PAF-2 (Figure S7), outperforming those of Nafion⁶¹ by roughly 1 order of magnitude and approach the values for liquid electrolytes⁶⁵ with the advantage of SPAF-2_x^{RH} not losing the form stability. One reason for the exceptionally high conductivities might be the open 3D pore structure of the framework,^{32,53} which enables oxonium ions and water molecules to move essentially unrestricted through the pore structure as previously suggested for SPAF-1.³⁵ Immersing SPAF-2_{0.3/0.5/0.8}¹⁰⁰ in liquid water led to slightly lower conductivities (Figure S21), which probably is a consequence of inhomogeneous pore filling. Thus, we focus on gas-phase equilibration for preparing the electrolyte-host system SPAF-2_x^{RH}.

While the conductivities at ambient temperatures are similar for all three sulfonation degrees at 100% RH, the activation barriers differ significantly. For *x* = 0.8, *E*_A is the largest with 59 kJ mol⁻¹, goes through a minimum at *x* = 0.5 (*E*_A ≈ 35 kJ mol⁻¹), and increases slightly for *x* = 0.3 (*E*_A ≈ 43 kJ mol⁻¹). Similar trends were also observed for 67 and 33% RH. The observation that *E*_A is the largest (≈60 kJ mol⁻¹) for *x* = 0.8, independently of RH, indicates that the high SO₃⁻ density introduces confinement effects, which influence the proton conductivity in all cases. Low sulfonation degrees of 30%, however, lead to low charge carrier concentrations and a reduced ability of the frameworks to swell upon water uptake. Consequently, the confinement changes, and oxonium ions and the water molecules within the pores are more strongly

affected by the negative framework charge. Optimal values of charge density, carrier concentration, water uptake, and framework swelling appear to be reached for medium sulfonation degrees of around *x* = 0.5.

Counterintuitively, the charge transport activation barriers do not change steadily with water uptake (Figure 2D). This can be explained, if more than one thermally activated process drives the charge transport. The corresponding *E*_A will exhibit different trends upon changing the confinement by adapting RH and *x*. To derive a better understanding of the nature of these processes temperature-dependent ¹H NMR spectroscopic line shape, spin–lattice relaxation, and SFG experiments were carried out for SPAF-2_{0.3}¹⁰⁰, SPAF-2_{0.5}¹⁰⁰, and SPAF-2_{0.8}¹⁰⁰.

H₃O⁺/H₂O Mobility and Diffusion. At low temperatures (≈ 220 K), the lineshapes of the ¹H NMR spectra for SPAF-2_{0.3}¹⁰⁰, SPAF-2_{0.5}¹⁰⁰, and SPAF-2_{0.8}¹⁰⁰ consist of three distinctly different components (Figure 3A). Two components are broad and were fitted with Gaussian profiles. Their full widths at half-maximum (fwhm) were found to be about 27 and 81 kHz, independent of the temperature. The third component is Lorentzian-type and narrow, with fwhm < 10 kHz. The Gaussian-type resonance with a fwhm of about 27 kHz is typical of a rigid SPAF-2 framework, where the shortest ¹H–¹H distances (*d* ≈ 2.4 Å) arise from neighboring protons at the aromatic rings. The fraction of this line shape component (dashed line, Figure 3A) is also temperature-independent (Figure 3B), indicating that the framework remains rigid between 220 and 380 K. The derived proportions (0.17 for SPAF-2_{0.8}¹⁰⁰, 0.18 for SPAF-2_{0.5}¹⁰⁰, and 0.28 for SPAF-2_{0.3}¹⁰⁰) match well the expected ¹H ratios for framework and water hydrogen atoms.

The two remaining resonances were assigned to adsorbed water molecules and oxonium ions. The broad Gaussian-type component (fwhm ≈ 81 kHz) is characteristic of water molecules immobilized at the inner pore surfaces. Its fwhm is roughly three times broader than that of the framework matching the expected ratio $\approx (d_{\text{HH}}(\text{SPAF-2})/d_{\text{HH}}(\text{H}_2\text{O}))^3$ with $d_{\text{HH}}(\text{H}_2\text{O}) \approx 1.6$ Å. The narrow and temperature dependent Lorentzian-type component results from mobile $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ within the pores, which show fast and almost isotropic reorientation. It narrows with the temperature suggesting that the reorientation becomes faster (Figures S22–S24 and Table S22).

In contrast, the fwhm of the broad Gaussian-type resonance does not change markedly, indicating that water molecules attached to the inner surfaces remain immobile. With increasing temperature, the fraction of the narrow component grows at the expense of the broad component, indicating that the mobile water fraction grows. For SPAF-2_{0.8} and SPAF-2_{0.5}, roughly 45% of the $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ are immobilized at 220 K, while already 90% of the water molecules move isotropically at 273 K (Figure 3B). Beyond 300 K, the broad Gaussian-component falls below the detection limit. For SPAF-2_{0.3}, where less water is adsorbed, the proportion of the broad Gaussian-component approaches zero already beyond 250 K. Based on the DSC experiments (Figure S5 and Table S8) a small part (<15%) of the water molecules might additionally be immobilized as ice inclusions below 260 K. As this does not change the trend of the line shape analysis we omitted the contribution for the following discussion.

This analysis suggests that two water fractions, which are well distinguished in terms of mobility, coexist inside the framework. The temperature dependence of the corresponding fractions is typical for these two ensembles to be in equilibrium. Thus, for the ^1H proportions for mobile ($p(\text{H}_2\text{O}_{\text{mo}})$) and immobile ($p(\text{H}_2\text{O}_{\text{im}})$) water molecules, it follows:

$$p(\text{H}_2\text{O}_{\text{im}}) = 1 - p(\text{H}_2\text{O}_{\text{mo}}) - p(\text{framework})$$

$$p(\text{H}_2\text{O}_{\text{mo}}) = \frac{1 - p(\text{framework})}{1 + e^{\Delta H^\circ/RT} \cdot e^{-\Delta S^\circ/R}} \quad (1)$$

$p(\text{framework})$ is the framework proportion and ΔH° and ΔS° are the enthalpy and entropy changes. Fitting the fractions displayed in Figure 3B with eq 1 revealed that the subensemble of immobile $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ is energetically favored by 15 to 25 kJ mol^{−1} compared to the mobile species, while the entropy for the immobile species is lower by 80–110 J mol^{−1} K^{−1} (Table S23). Due to the low contributions of the immobile species for SPAF-2_{0.3}¹⁰⁰ for the corresponding refinement, ΔS° was restricted to an average of 90 J mol^{−1} K^{−1}. We attribute the lower enthalpy for the immobilized $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ species to attractive interactions with the SO_3^- groups. The higher entropy of the mobile fractions accounts for the higher motional degrees of freedom and an increasing disorder.

^1H NMR SFG spectroscopy allows for probing the diffusivity and thus the long-range transport of the mobile subensemble. Considering that compared to each acidic proton from a sulfonic acid group, 10–14 water molecules are adsorbed depending on x , the ^1H SFG NMR spectroscopic signal is dominated by the diffusion of adsorbed water molecules. As the spin–lattice relaxation (Figure S28) is very short (400 $\mu\text{s} \leq T_1 \leq 1$ ms), we could collect reliable ^1H SFG NMR data only for SPAF-2_{0.3}¹⁰⁰ and SPAF-2_{0.8}¹⁰⁰ (Figure 3C). In both cases,

intriguingly large values of the self-diffusion coefficients D were observed, which are almost 2 orders of magnitude larger than those of water in other porous materials with similar pore sizes^{44,67} and only 1 order of magnitude lower than those of liquid bulk water.⁶⁶ We attribute this to the framework's open, interconnecting 3D pore space,^{32,53} which allows for unhindered diffusion despite the narrow pore sizes. The confined nature of the water molecules, nevertheless, becomes obvious considering the larger activation barriers (27 kJ mol^{−1} $\leq E_A \leq 33$ kJ mol^{−1}) compared to those of bulk water.

Further insight was obtained from ^1H spin–lattice relaxation data. The magnetization recovery is biexponential for SPAF-2_{0.3}¹⁰⁰, SPAF-2_{0.5}¹⁰⁰, and SPAF-2_{0.8}¹⁰⁰ for all temperatures. This makes a significant contribution from ice inclusions below 260 K unlikely (Figures S25–S27). The proportions of both components rather match the ratio for protons of the framework and adsorbed aqueous phase (Figure S29). The framework T_1 is a few tens of milliseconds and hardly temperature dependent (Figure S28). T_1 for the aqueous phase exhibits minima at 290 K (SPAF-2_{0.8}), 295 K (SPAF-2_{0.5}), and 320 K (SPAF-2_{0.3}), indicating dynamics on the nanoseconds scale ($\approx 1/\omega_0$) at these temperatures. However, the remarkably short T_1 values between 400 μs and 1 ms cannot be explained based on the ^1H – ^1H dipolar coupling constants of water molecules (≈ 80 kHz) as derived from the line shape analyses (Figure 3A). To match the T_1 minima, 10 times larger coupling constants are required, which is unrealistic based on nuclear spin interactions.⁶⁸

Considering, that small contents of oxidized Pd and Fe impurities are trapped in the framework (Table 1), it is likely that the spin–lattice relaxation is driven by heteronuclear dipole interactions between these paramagnetic centers and the protons of mobile $\text{H}_2\text{O}/\text{H}_3\text{O}^+$. In this case, T_1 exclusively probes their short-range translational motion with respect to these centers,⁶⁹ which we describe using the hydrodynamic force-free hard sphere (FFHS) model.⁷⁰ Further details are given in the Supporting Information. The FFHS model yields a spectral density $J_{\text{trans}}(\omega, \tau_{\text{trans}})$ (eq S4), which describes the fluctuations of the dipole interactions caused by the translational motion and involves a coupling constant C , which depends on the number density N_S of the paramagnetic centers, their spin state S , and the shortest possible distance d between paramagnetic centers and water molecules. In this case, T_1 is given by

$$\frac{1}{T_1} = C \cdot J_{\text{trans}}(\omega_1, \tau_{\text{trans}}) \quad (2)$$

Modeling the spin–lattice relaxation data (Figure S28 and Table S24) with eq 2 allowed us to determine the temperature-dependent correlation times τ_{trans} (Figure 3D) for all three samples. The trends for τ_{trans} suggest thermally activated translational motion with similar E_A values between 33 and 35 kJ mol^{−1} for $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ for all SPAF-2_x. These values are in excellent agreement with E_A derived from the diffusion data, confirming that T_1 relaxation and SFG NMR spectroscopy both probe water self-diffusion. The mean distance $\langle r \rangle = \sqrt{6D\tau_{\text{trans}}}$ (Figure 3C inset), thus decodes the length scale over which a water molecule diffuses before losing the correlation to a paramagnetic center. $\langle r \rangle$ is hardly temperature-dependent and varies between 2 nm (SPAF-2_{0.8}) and 5 nm (SPAF-2_{0.3}). The somewhat larger correlation length for SPAF-2_{0.3} is reflected in a larger τ_{trans} compared to SPAF-2_{0.5}

and SPAF-2_{0.8}, which show almost identical τ_{trans} . For a closed packing for the centers $N_S = 4(\sqrt{2}\langle r \rangle)^{-3}$, $\langle r \rangle \approx 3.5$ nm corresponds to a number density of $3 \times 10^{25} \text{ m}^{-3}$. This matches well the observed Pd and Fe contents (Table 1), strengthening our ansatz to describe T_1 by fluctuations of heteronuclear dipole interactions caused by diffusing H₂O/H₃O⁺ groups along the paramagnetic centers in the framework.

Conduction Mechanism. Using τ_{trans} and $\langle r \rangle$ (Figure 3C,D), we predict self-diffusion coefficients $D = \langle r \rangle^2 (\tau_{\text{trans}} \cdot 6)^{-1}$ for SPAF-2_{0.5}, where the spin–lattice relaxation was too fast to perform SFG NMR experiments. Thus, temperature-dependent D_s could be derived for SPAF-2_{0.3}¹⁰⁰, SPAF-2_{0.5}¹⁰⁰ and SPAF-2_{0.8}¹⁰⁰. Applying the Nernst–Einstein relation $\sigma_x^{\text{NMR}} = n_x \cdot e^2 \cdot D (k_B T)^{-1}$ allows for predicting conductivities based on the temperature-dependent diffusion coefficients for SPAF-2_{0.3}¹⁰⁰, SPAF-2_{0.5}¹⁰⁰ and SPAF-2_{0.8}¹⁰⁰. The corresponding proton number densities n_x are given in Table S25.

The values of σ_x^{NMR} and σ_x^{EIS} match well (Figure 4A). As the ¹H SFG and T_1 data are mainly sensitive to the diffusion of the water molecules, this suggests that protons are carried by water molecules according to a vehicle mechanism. Despite the high IECs, this observation rules out a packed acid mechanism, where charge transport is mediated by H⁺ hopping between neighboring SO₃[−] units without significant water transport.²⁰ As T_1 relaxation, SFG NMR and EIS probe translational motion on length scales ranging from a few nanometers up to a few micrometers, the transport mechanism is length scale independent. This renders the influence of bottleneck effects unlikely.

However, while similar E_A of about 35 kJ mol^{−1} were found for $\sigma_{0.5}^{\text{NMR}}$ and $\sigma_{0.5}^{\text{EIS}}$, the activation barriers of $\sigma_{0.3}^{\text{EIS}}$ and $\sigma_{0.8}^{\text{EIS}}$ are roughly twice as high compared to the ones derived from $\sigma_{0.3}^{\text{NMR}}$ and $\sigma_{0.8}^{\text{NMR}}$ (Figure 4B). For the latter two compounds, $\sigma_x^{\text{EIS}} < \sigma_x^{\text{NMR}}$ at low temperatures, while the opposite trend is established above ≈ 320 K (SPAF-2_{0.8}) and ≈ 350 K (SPAF-2_{0.3}). H⁺ transport exceeding the diffusivity of water molecules might hint toward contributions of a Grotthuss-like mechanism.¹⁹ However, the high E_A for σ_x^{EIS} and the strong confinement by the framework make this unlikely. The small pore size suppresses the necessary formation of Zundel and Eigen ions, as water molecules within three solvation shells around one oxonium ion need to be positioned and aligned.²²

Considering the results of the ¹H NMR analysis, an alternative scenario is much more likely. Confining H₂O and H₃O⁺ within the framework led to the formation of two subensembles (Figure 3A,B). In addition to water molecules and oxonium ions that are immobilized in the vicinity of the SO₃[−] groups, highly mobile species were observed even at temperatures far below RT (Figure 4C). The temperature dependence of their proportions revealed similar energetic differences of about 20 kJ mol^{−1} for all sulfonation degrees (Table S23). As the immobile and mobile species are spatially close and both subensembles relax with the same T_1 component (Figures S25–S27), we expect a continuous exchange of H₂O and H₃O⁺ between both subensembles (Figure 4C). Water molecules and oxonium ions, immobilized at a particular time, will become mobile, or vice versa. The corresponding exchange rates κ are on the order of 10⁴ Hz, as κ is small enough ($< 10^6$ Hz) for the line shape analyses to be in the slow exchange limit and large enough ($> 1/T_1 \approx 10^3$ Hz) to allow both subensembles to relax with the same spin–lattice relaxation rate. Due to exchange between both subensembles,

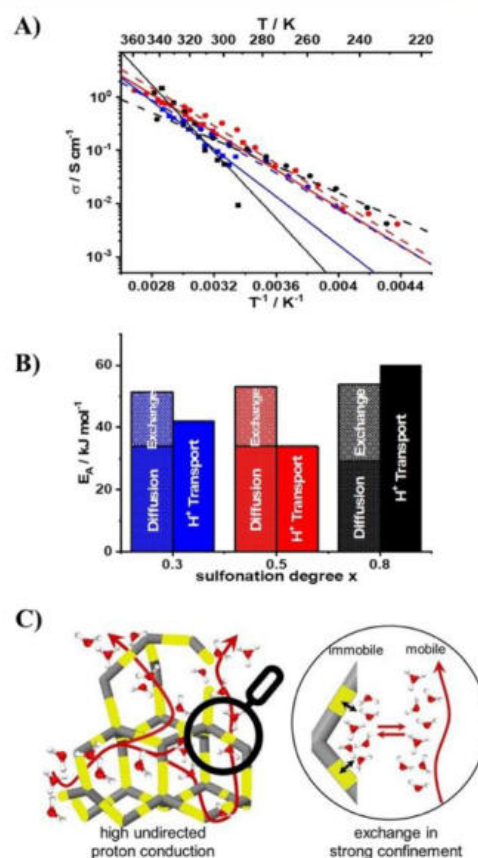


Figure 4. (A) Comparison of proton conductivities σ for SPAF-2_{0.3}¹⁰⁰ (blue), SPAF-2_{0.5}¹⁰⁰ (red), and SPAF-2_{0.8}¹⁰⁰ (black). Solid squares are used for data obtained with EIS. σ values derived from the ¹H SFG NMR ($x = 0.3$ and 0.8) and T_1 relaxation data ($x = 0.5$) using the Nernst–Einstein relation are depicted as solid circles. The lines (dashed for σ_x^{NMR} and solid for σ_x^{EIS}) are guides for the eye. (B) Comparison of activation barriers derived from the NMR spectroscopy and EIS data. (C) Schematic representation of a cutout of the molecular structure of SPAF-2_x using an ideal diamond lattice. The yellow areas symbolize hydrophilic regions around the SO₃[−] units, and the gray areas represent hydrophobic regions. Zoom: Schematic presentation of the proposed mechanism for the charge transport for SPAF-2_{0.5}¹⁰⁰, which involves an exchange between mobile and immobilized water molecules.

the total activation barrier for the charge transport is the sum of the exchange enthalpy and the activation barrier for the diffusion (Figure 4B).

Thus, the proposed H⁺ transport mechanism is a combination of periods where fast transport by diffusion occurs and periods where the same water molecules and oxonium ions become reversibly attached to the framework by electrostatic interactions (Figure 4C). The continuous exchange between two distinct, in terms of enthalpy and entropy well separated, aqueous regions sets the H⁺ transport in SPAF-2_{0.3}¹⁰⁰ apart from other materials like Nafion and sulfonated mesoporous silica^{11,21,27} where usually homogeneous models with distributions of activation barriers apply. We attribute this difference to the strong confinement effects imposed on the aqueous phase by the narrow micropores. Due

to the 3D framework with its interpenetrating, windowless pore space, the slowdown of molecular diffusion, which usually results from strong confinement, is prevented. Despite the larger pore volumes water diffusion is slower by up 3 orders of magnitude for porous materials mentioned earlier.^{11,21,27} Combining the extraordinary diffusivity within the confined aqueous phase of SPAF-2¹⁰⁰ with IECs up to 5.7 mequiv g⁻¹ and the exchange between framework-attached and free H₂O/H₃O⁺ species allows for excellent conductivities between 0.5 and 2.0 S cm⁻¹ (Figures 2C and 4A).

The trends for E_A as a function of the sulfonation degree determined from σ_x^{EIS} and the NMR experiments (Figure 4B) suggest that the framework polarity influences the exchange process. For $x = 0.3$ and 0.8, water molecules and oxonium ions participate in the exchange, as E_A determined for the charge transport (EIS) is significantly higher than E_A of the diffusion and T_1 data. In contrast, for $x = 0.5$, both E_A match, suggesting that only water molecules are immobilized at the SO₃⁻ groups, while the oxonium ions remain preferentially in the mobile phase.

We attribute this phenomenon to the distribution of sulfonic acid groups as the hydrophobic framework becomes hydrophilic in the vicinity of the SO₃⁻ units. Additionally, the induced electrostatic interactions provide the necessary restraint for immobilizing H₂O/H₃O⁺. To probe repeating, characteristic distances, wide-angle X-ray scattering (WAXS) experiments were carried out in a Q range that corresponds to distances between 1.7 and 7.4 Å (Figure 5). As the frameworks swell upon water uptake influencing the alignment of the

framework racks, the measurements were carried out in conditions where the water uptake could be controlled. Since the adsorbed water molecules are mobile and distributed in the pores, they will lead to smooth and slowly modulating scattering intensities. Sharper modulations can be attributed to the framework and the sulfonic acid groups. The diffractograms are similar for SPAF-2¹⁰⁰_{0.3} and SPAF-2¹⁰⁰_{0.8}, with distances around 5 Å occurring most frequently (Figure 5). Such distances match those of SO₃⁻ groups and neighboring benzene rings. For SPAF-2¹⁰⁰_{0.5}, a prominent maximum of around 3.3 Å instead occurs, hinting at SO₃⁻ groups attached predominantly to the sandwiched benzene rings. This indicates a higher order for medium SO₃H contents.

For sulfonation degrees of 0.3, 0.5, and 0.8, on average, two, three, and five of the six benzene rings of the repeating unit are sulfonated. Larger patches of unsulfonated and, thus, hydrophobic regions remain for $x = 0.3$ (Figure 5). For $x = 0.8$, almost the whole framework is hydrophilic. In both cases, the interpretation of the WAXS data suggests a disordered arrangement of sulfonate groups as the dominating peak is explained well with the framework—SO₃⁻ contacts. For $x = 0.5$, the SO₃⁻ groups are preferentially attached to the middle benzene units of the racks. This leads to alternating hydrophobic and hydrophilic regions (Figure 5) and might be a consequence of the Coulomb repulsion between the negatively charged SO₃⁻ units and the reversibility of sulfonation during synthesis.

A regular placing of SO₃⁻ units for $x = 0.5$ (Figure 5) leads to mean O—O distances that selectively attract water molecules in double hydrogen bonds, while oxonium ions do not match. This provides a reasonable explanation for the preferential immobilization of water molecules and lower activation barriers ($E_A \approx 35$ kJ/mol) for the charge transport in this case. For $x = 0.3$ and 0.8, unspecific adsorption takes place which influences both water molecules and oxonium ions alike. Optimal proton conductivities are a subtle trade-off between surface interactions, water uptakes, and proton densities where optimal conditions are reached for medium-high sulfonation degrees around $x = 0.5$.

CONCLUSIONS

We report the synthesis and characterization of SPAF-2 _{x} . It is a flexible, amorphous, and nanoporous framework that can be prepared with varying sulfonation degrees x . The prepared systems ($x = 0.3, 0.5$, and 0.8) take up roughly their own weight in water when saturated at 100% RH. More than 85% of the adsorbed water molecules are located in micropores, which induces strong confinements for the adsorbed fluid phase. Strong interactions with covalently bound SO₃⁻ units and IECs up to 5.7 mequiv g⁻¹ promise highly efficient electrolyte-host systems with an improved water management toward higher temperatures and less hindrance due to ice formation below 0 °C.

Outstanding DC conductivities of about 1 S cm⁻¹ could be realized for systems saturated at 100% RH, which surpass conductivities reported in related frameworks with similar pore sizes by 1–2 orders of magnitude (Table S1). Bulk and grain boundary transport become indistinguishable which we attribute to the formation of a continuous fluid phase including pore and particle-surface water. Although similar proton conductivities were found for low ($x = 0.3$), medium ($x = 0.5$), and high ($x = 0.8$) sulfonation degrees at elevated temperatures (≈ 353 K), the activation barriers of the charge

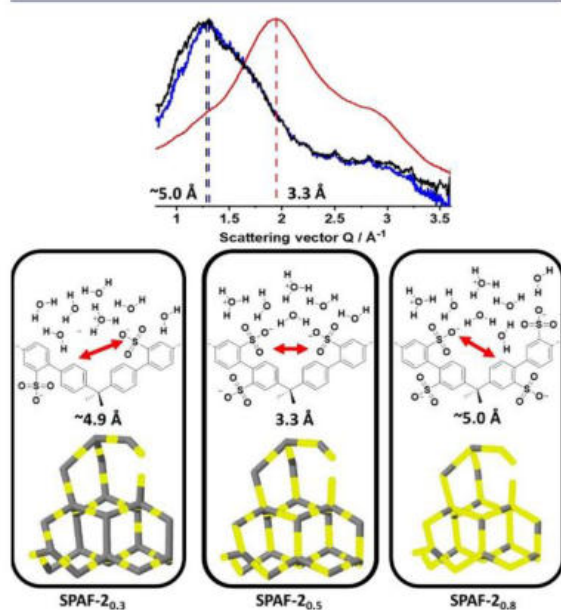


Figure 5. Top: WAXS measurement of SPAF-2¹⁰⁰_{0.3} (blue), SPAF-2¹⁰⁰_{0.5} (red), and SPAF-2¹⁰⁰_{0.8} (black) with vertical lines highlighting the most frequently occurring distances. Deconvolutions are given in Figure S30. Schematic representation of a likely local structural arrangement of SPAF-2 _{x} . The yellow areas symbolize hydrophilic regions around the SO₃⁻ units, and the gray areas represent hydrophobic regions. The red arrows point to typical framework distances that match the experimentally observed ones.

transport vary. Minimal values at medium sulfonation degrees provide the broadest temperature range for application as high-performance electrolyte-host material. This makes SPAF-2_{0.5}¹⁰⁰ promising for fabricating proton-conducting membranes used at variable temperatures between 233 and 353 K. In this range, proton conductivities vary between 0.01 and 1 S cm⁻¹.

The underlying transport processes are based on a vehicle mechanism with exceptionally high self-diffusion coefficients of about 10⁻⁹ m² s⁻¹ for water molecules adsorbed in the nanometer-sized pores at RT. This surpasses the diffusivity in common micro- and mesoporous systems by up to 3 orders of magnitude. We explain this result by the open, windowless 3D pore structure of the SPAF-2 frameworks, enabling an almost unhindered diffusion despite strong confinement. The highly mobile water molecules and oxonium ions are in a continuous exchange with counterparts that strongly interact with the SO₃⁻ units of the framework. Water molecules and oxonium ions in this subensemble exhibit a reduced mobility and lower energy compared to those in the mobile subensemble that hardly interacts with the framework. Both subensembles are in thermal equilibrium and exchange water and oxonium ions on the order of milliseconds. When the temperature is increased, the high-energy population grows at the expense of the low-energy population, and hence, a larger number of molecules has enough thermal energy to take part in the charge and mass transport. The higher local order for the distribution of sulfonate groups for medium sulfonation degrees intriguingly leads to preferential immobilization of water molecules while the oxonium ions remain in the fluid phase. This reduces the transport barriers as oxonium ions are less likely immobilized at the framework, extending the temperature range where SPAF-2_{0.5}¹⁰⁰ exhibits high proton conductivities.

We show how the strong confinements imposed by nanoporous hosts on the imbedded electrolyte phase fundamentally change the mechanisms for mass and charge transport. Despite the additional restraints imposed by strong confinement, we demonstrate that it can positively impact and improve the conductivity. Maximizing the sulfonate density and IEC is less important than maximizing the framework topology, the host–guest interactions, and the sulfonate arrangement. This knowledge will help to tailor porous polymers and COFs for electrolyte-host systems with liquid-like conductivities in the future.

EXPERIMENTAL SECTION

All chemicals and solvents used in the synthesis were commercially available and were of reagent grade without further purification. Air-sensitive reactions were carried out under Ar (purity 5.0) atmosphere which passed a zeolite, P₂O₅, and BTS catalyst column. The syntheses of TPM, BrTPM, PAF-2, and SPAF-2_x are described in detail in the Supporting Information. To load the SPAF-2_x frameworks with a controlled water amount, the samples were equilibrated for up to 48 h in a humidity chamber at 33, 67, and 100% RH, respectively, using saturated salt solutions or water. Further activation was not necessary.

Physisorption measurements with Ar as adsorbate were carried out on an Autosorb I at 87 K. Water physisorption measurements were performed on an ASI-Q-MP-MP-AG setup (Anton Paar Quantatec, Boynton Beach, USA) at 293 K. Before the measurements, all samples were degassed at 393 K for 12 h. The software package ASI-Q ver. 3.0 was used for data analysis. The ¹H and ¹³C liquid-NMR spectra of the synthesized molecules were measured on a Bruker 500 MHz spectrometer and using dimethyl sulfoxide as solvent. IR spectra were recorded on a JASCO FT/IR-6100 Fourier-transform IR spectrometer with an attenuated total reflectance unit.

CHNS analysis was measured on an ELEMENTAR UNICUBE with sulfanilamide as standard.

For DSC, the samples were saturated at 33, 67, and 100% RH. The measurements were done on a TA Instruments Discovery DSC 2500. The temperature range was 193 to 353 K with 5 K min⁻¹ under a nitrogen atmosphere and three heating cycles. For evaluation, the third cycle was used. TGA was carried out on a Mettler Toledo TGA/SDTA851e under a nitrogen atmosphere in the temperature range from 303 to 973 K with a heating rate of 10 K min⁻¹. TGA-MS was performed on a Netzsch STA 449 C (TGA) with a Netzsch Aeolos QMS 403C (MS) under a nitrogen atmosphere with a heating rate of 5 K min⁻¹. To determine the sulfonation degree the samples were titrated with a Mettler Toledo seven2go pH meter and an aqueous 10 mM NaOH solution.

Powder X-ray diffraction was done on a STOE STADI P diffractometer with a Ge(111) monochromator and Cu-K_{α1} radiation. The frameworks were packed in 1.0 mm capillaries and were measured at RT in Debye–Scherrer geometry. WAXS measurements were performed using a Xeuss 3.0 (Xenocs, France) equipped with a copper source (λ = 1.5418 Å). Scattering images were detected on an Eiger2 R 1 M detector (Dectris, Switzerland) with 1028 × 1062 pixels and a pixel size of 75 μm × 75 μm located 0.3 m from the sample (deducted via AgBeh calibration). The beam size was 0.5 mm × 0.5 mm. Each sample was equilibrated at 100% RH, sealed Kapton containers, and measured for 1 h. The WAXS images were radially averaged to extract 1D cuts and background corrected (empty container). Peak positions were determined by fitting each peak profile with a local background and a Gaussian function using XTRACT 2.0 (Xenocs, France).

All solid-state NMR spectra were recorded on a Bruker Avance III HD spectrometer with a B₀ field of 9.4 T. ¹H and ¹³C MAS spectra were performed with a ramped cross-polarization experiment in which the nutation frequency ν_{nut} on the proton channel was varied linearly from 70 to 100%. The sample was rotated with a frequency of 12.5 kHz (¹³C) in a 3.2 mm MAS double-resonance probe (Bruker). The corresponding ν_{nut} values on the ¹³C channel and the contact time were set to 70 kHz and 1.0 ms, respectively. Proton broadband decoupling with Spinal-64 and ν_{nut} = 60 kHz was performed during acquisition. ¹³C spectra were referenced to tetramethylsilane using adamantane as a secondary standard. Single-pulse experiments were performed with a single 90° pulse. The pulse length was 3.20 μs, and the recycle delay was set to 120 s. The spin–lattice relaxation was characterized using an inversion recovery sequence with a leading 180° pulse of 3.5 μs.

In the ¹H SFG NMR experiments, the magnetic field gradient *g* was generated by a specially designed magnet with superconducting coils in anti-Helmholtz arrangement.⁷¹ We placed the sample at a position with an ¹H Larmor frequency of 173 MHz and used two gradients of magnetic field *G* = 132 T m⁻¹ and *g* = 76 T m⁻¹. The stimulated-echo sequence, which features two evolution times *t_e* separated by a mixing time *t_m*, was applied to measure the ¹H self-diffusion coefficients *D*. Explicitly, the stimulated-echo decays were fitted to

$$S(t_m, t_e) \propto e^{-Dq^2 t_d} \quad (3)$$

Here, *t_d* = *t_m* + 2/3 *t_e* is the variable diffusion time, and *q* = *g**t_e* with *γ* being the gyromagnetic ratio. The length of the 90° pulses was 0.7 μs. In all measurements, the temperature was set with an accuracy of ±1 K and stabilized to ±0.1 K using a nitrogen flow cryostat.⁷¹

For the conductivity measurements, the sample was placed in the sample holder under continuous gas flow with the set humidity of 33, 67, or 100% RH. For comparison a set of dried samples was immersed in liquid water. The water amount was estimated based on physisorption (Figure 1A) for *p*/*p*₀ = 1 allowing for an excess of 10%. After immersion, excess water was evaporated at room temperature against air. The water loss was controlled on a scale. When the weight was reached, the samples were sealed and equilibrated for an additional 3 days. Impedance spectroscopy was performed on a Novocontrol Alpha Analyzer with ZG4 and a 5 mV AC voltage was applied. An impedance data set was prepared to

measure the frequency range from 4 MHz to 1 Hz. To ensure the same shape and size of the pellet during measurement, the sample was placed in a cylindrical border with an active radius of 4 mm. Two copper electrodes were placed adjacent to the top and bottom of the pellet and with constant pressure of about 200 bar. The atmosphere was stable to the set value during the measurement. To ensure equilibration of the temperature, the conductivity measurement was started 30 min after the appropriate temperature. After the measurements had been made, the length (l) of the pellet was measured. From the determined lengths and $A = \pi r^2$ with $r = 4$ mm, the conductivity was calculated according to the formula $\sigma = l(A \cdot R)^{-1}$, where R is the resistance from the high-frequency semicircle in the corresponding Nyquist plot (Cole plot). This was simulated with an equivalent circuit diagram consisting of at least one resistor R and a constant phase element connected in parallel in RelaxIS 3.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c09257>.

Proton conductivities of similar porous materials for comparison, synthesis protocols, additional information on framework characterization including, elementary analysis, titration curves, EDX, TGA, IR and NMR spectroscopy, pore size distributions for PAF-2 and SPAF-2_{SO3H}, DSC thermograms for SPAF-2_{SO3H}, EIS spectra and refinement parameters, ¹H line shape analyses, T_1 relaxation data and refinement parameters, WAXS data, and deconvolution (PDF)

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Author Contributions

[†]In memoriam to our dear colleague; unexpectedly deceased on November first 2022.

Author Contributions

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■ ABBREVIATIONS

PMFC	polymer membrane fuel cell
MEA	membrane electrolyte assembly
IEC	ion exchange capacity
RH	relative humidity
POM	polyoxometalate
MOF	metal–organic framework
POF	porous organic framework
PAF	porous aromatic framework
SPAF	sulfonated porous aromatic framework
FTIR	Fourier-transform infrared
NMR	nuclear magnetic resonance
EA	elemental analysis
EDX	energy-dispersive X-ray
TGA	thermal gravimetric analysis
DSC	differential scanning calorimetry
BrTPM	tetrakis(4-bromophenyl)methane
BDB	benzene-1,4-diboronic acid
SP	single-pulse
BET	Brunauer–Emmett–Teller
TGA-MS	thermal gravimetric analysis mass spectrometry
SA	surface area

DFT	density functional theory
IUPAC	international union of pure and applied chemistry
ESEM	environmental scanning electron microscope
EIS	electrochemical impedance spectroscopy
B	bulk
GB	grain boundaries
E	electrode
EI	electrode interface
fwhm	full widths at half-maximum
SFG	static-field gradient
DC	direct current
WAXS	wide-angle X-ray scattering
FFHS	force-free hard sphere

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Supplementary Materials for

**Ultrafast proton conduction in an aqueous electrolyte
phase confined in adamantane-like micropores of a
sulfonated, aromatic framework**

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† In memoriam to our dear colleague; unexpectedly deceased on November 1st 2022

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Conductive frameworks from literature

Table S1. Overview of electrolyte-host systems based on MOFs, COFs and PPs including pore sizes and conductivities.

framework	pore size / Å	conductivity / S cm ⁻¹	conditions		ref.
			RH / %	T / K	
NUS-9 (R)	14	$1.24 \cdot 10^{-2}$	98	296	1
NUS-10 (R)	14	$3.96 \cdot 10^{-2}$	98	296	1
Ox-BD-COF-SO ₃ H	30	$1.79 \cdot 10^{-6}$	98	363	2
SPAF-1	~10	$1.6 \cdot 10^{-1}$	95	353	3
PyTTA-DHTA-COF-SO ₃ H	17	$2.0 \cdot 10^{-2}$	100	343	4
PCF-1-SO ₃ H	--	$2.6 \cdot 10^{-2}$	95	343	5
HOF-GS-11	11	$1.8 \cdot 10^{-2}$	95	303	6
TpPa-SO ₃ H	14	$1.02 \cdot 10^{-1}$	100	383	7
S-POP-BP-1	~10	$4.6 \cdot 10^{-3}$	95	298	8
S-POP-BP-TPOT	~15, ~30	$1.5 \cdot 10^{-2}$	95	298	8
SBO-CMP-1	< 20	$1.29 \cdot 10^{-2}$	100	343	9
MPOPS-1	13	$3.07 \cdot 10^{-2}$	100	353	10
1S	6	$7.72 \cdot 10^{-2}$	90	353	11

Synthesis and Characterization of PAF-2 and SPAF-2_x

PAF-2

1.3166 g (2.07 mmol, 1 eq.) tetrakis(4-bromophenyl)methane, 687.5 mg (4.14 mmol, 2 eq.) benzene-1,4-diboronic acid, 95.7 mg (82.8 μmol, 0.04 eq.) Pd(PPh₃)₄ and 34.6 mg (82.8 μmol, 0.04 eq.) 1,1'-bis(di-*i*-propylphosphino)ferrocene (dippf) are placed in a vessel under Ar atmosphere and dissolved with 340 ml degassed THF and 41 ml degassed 2 M K₂CO₃. The solution is stirred for 20 h under reflux (64°C). The resulting solid is filtered and washed two times with THF, water, and EtOH. Further purification is done via Soxhlet equipment with THF and water (1:1) for 16 h. The beige solid is dried under reduced pressure at 150 °C. The yield was 926.6 g corresponding to 1.98 mmol (96 %). The purity was verified by EA, EDX, IR, and solid-state NMR spectroscopy (Figures S1A, S1D, and Table S3)

SPAF-2_x

In a frit 120 mg of dry PAF-2 are stored. A flask is connected to the bottom of the frit, the top is connected to the vacuum line. After degassing the setup, fuming sulfonic acid is given in the flask. The plug is opened to vacuum for the allowed time (30 s, 60 s, 90 s). After the sulfonation time, the plug was opened to argon, and the gas was led through the sample and purified with ethanol Soxhlet. The sample is dried under reduced pressure. The yields were 139.4 mg ($x = 0.3$), 161.8 mg ($x = 0.5$), and 192.4 mg ($x = 0.8$) corresponding to 0.23 mmol (91 %), 0.24 mmol (94 %), and 0.22 mmol (87 %). The purity was verified by EA, EDX, IR, and solid-state NMR spectroscopy (Figures S1A, S1D, and Tables S4-6).

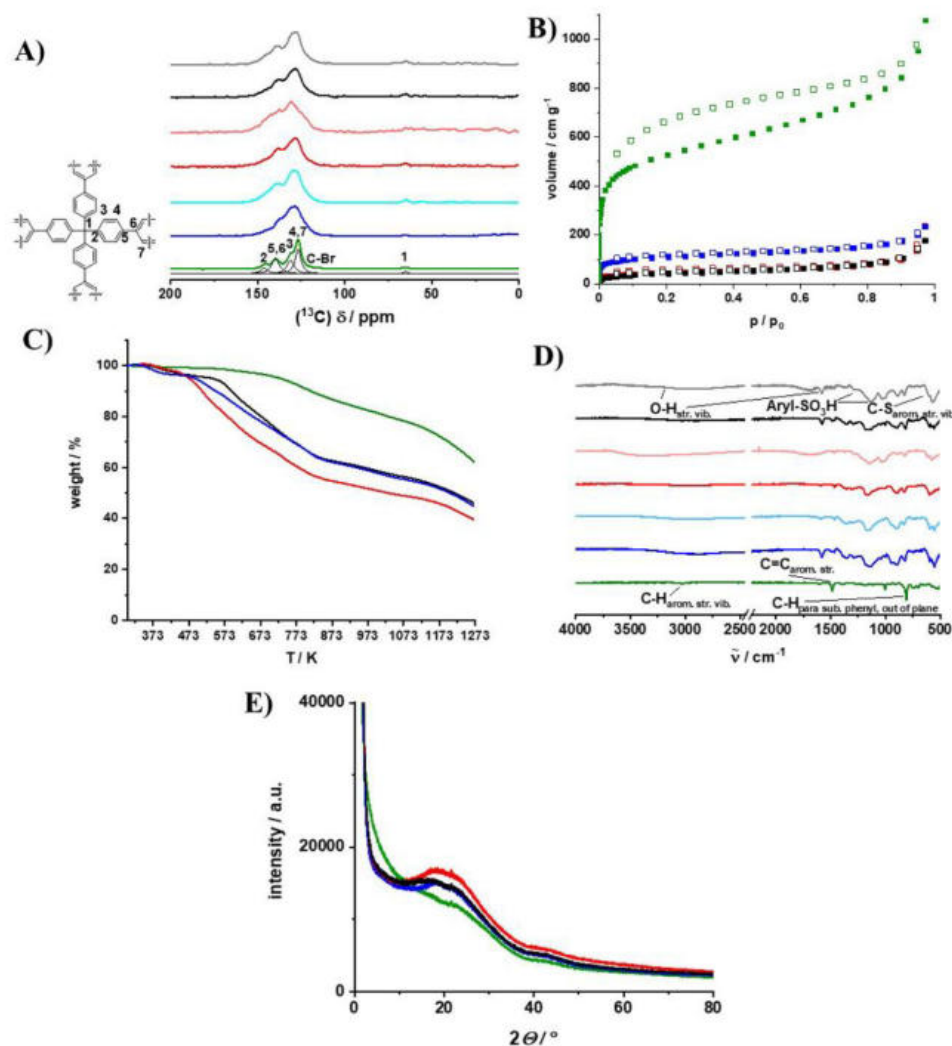


Figure S1. NMR and IR spectra, Ar isotherms and TGA curves and diffractogram of PAF-2 (green), SPAF-2_{0.3} (blue), SPAF-2_{0.5} (red), SPAF-2_{0.8} (black) after synthesis and SPAF-2_{0.3} (light blue), SPAF-2_{0.5} (light red) and SPAF-2_{0.8} (grey) after performing the temperature-dependent EIS and NMR spectroscopy measurements to verify the long-term stability of the sulfonated frameworks. A) ¹³C SP MAS NMR spectrum of PAF-2 and ¹³C CP MAS NMR spectra of SPAF-2_x with assignment. For the spectrum of PAF-2, additionally, a deconvolution is shown. B) Ar physisorption measurements at 87 K and C) TGA measurements in air. D) IR spectra of PAF-2 and SPAF-2_x. E) X-ray powder pattern of PAF-2 and SPAF-2_x.

Table S2. Refinement parameters of the deconvolution of the ^{13}C SP NMR spectrum of PAF-2 with pseudo-Voigt functions (Figure S1A bottom).

Signal	1	2	3	4, 7	5, 6	C-Br
Chemical shift / ppm	64.9	146.1	131.1	126.7	139.7	121.0
Integral	1.00	3.36	6.73	14.58	11.59	0.93
LB	284.4	428.7	536.0	420.0	525.8	457.4
G/L	0.746	0.000*	1.000*	0.306	0.011	0.282

*The Gauß-Lorenz ratios were kept constant during the refinement.

The successful cross-coupling reaction to PAF-2 is shown by the formation of the C-C bond of the carbon atoms **5** and **6** (Figure S1A). The ^{13}C NMR resonance at 140 ppm (Figure S1A) and the aromatic stretching vibration at 1487 cm^{-1} compared with the out of plane bending vibration for para-substituted phenyl at 808 cm^{-1} are clearly visible in the FTIR spectra (Figure S1D). To quantify the bond formation a quantitative single-pulse (SP) ^{13}C MAS NMR spectrum was acquired and deconvoluted (Figure S1A bottom and Table S2). The weak resonance at 121 ppm typical of aromatic C-Br end groups shows that a major part of the TBPM precursor was successfully incorporated into the framework. Its one-to-one ratio with resonance **1** indicates a cross-linking degree of about 80(5) %. As the C-Br end group resonance is superimposed by signals of the aromatic C-H resonances (**4**, **7**, Figure S1A), this value likely represents a lower limit. Additionally, the cross-linking degree was determined by EA and EDX (Table S3) with roughly 95 %. These three cross-linking degrees give an average of 90 %.

Small proportions of about 0.02 at.-% palladium and 0.08 at.-% iron were additionally detected. They are residuals of the used catalysts of the cross-coupling reaction and will occur most likely in an oxidized form as paramagnetic Pd^{2+} and Fe^{3+} . The fact that these impurities could not be removed by subsequent processing and Soxhlet extraction suggests an immobilization within the framework.

After sulfonation the characteristic aromatic bending and stretching vibrations for PAF-2 (808 cm^{-1} , 1487 cm^{-1} , Figure S1D), as well as the typical aliphatic and aromatic ^{13}C NMR resonances (64 ppm, 120-140 ppm, Figure S1A), do not change, indicating that the framework remains intact. Additional vibrations at about 610, 1200, and 1285 cm^{-1} were observed, which are typical for C-S aromatic stretching and aryl sulfonic acid vibrations. They prove the covalent attachment of the sulfonic acid groups to the aromatic spacers.

Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework

Table S3. Composition calculated from EA and EDX normalized to 37 C atoms corresponding to the repeating unit of PAF-2.

<i>PAF-2</i>		<i>C</i>	<i>H</i>	<i>Fe</i>	<i>Pd</i>	<i>Br</i>
Composition	at.-%	37	24	0.08	0.02	0.1
<i>EA</i>	wt.-%	85.12	4.68	--	--	--
	at.-%	7.09	4.64	--	--	--
	Normalized to 37 C atoms at.-%	37	24.24	--	--	--
<i>EDX</i>	at.-%	93.0	--	0.05	0.2	0.2
	Normalized to 37 C atoms at.-%	37	--	0.08	0.02	0.1

Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework

The average stoichiometry of the repeating units of the three SPAF-2 derivatives was determined by combining results of EA, EDX analysis, and titration (Table 1). These results support the spectroscopic findings that the framework structure does not change upon sulfonation. In particular, the C-Br end groups do not react with SO₃ leading to a constant bromine content for all samples. Neither the sulfonation nor subsequent processing change the Pd/Fe content of the samples markedly.

Table S4. Composition calculated from EA, EDX, and titration normalized to 37 C atoms corresponding to the repeating unit of SPAF-2_{0.3}.

SPAF-2_{0.3}		C	H	N	S	Br
Composition	at.-%	37	25.1	--	1.8*	0.1
<i>EA</i>	wt.-%	59.48	3.39	0.19	13.14	--
	at.-%	4.95	3.36	0.01	0.41	--
	Normalized to 37 C atoms at.-%	37	25.13	0.10	3.06	--
<i>EDX</i>	at.-%	79.1	--	--	3.7	0.3
	Normalized to 37 C atoms at.-%	37	--	--	1.7	0.1
<i>Titration</i>	Normalized to 37 atoms at.-%	37	--	--	1.8	--

*The sulfur content was calculated from titration curve displayed in Figure S3A.

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Table S5. Composition calculated from EA, EDX, and titration normalized to 37 C atoms corresponding to the repeating unit of SPAF-2_{0.5}.

SPAF-2_{0.5}		C	H	N	S	Br
Composition	at.-%	37	39.0	--	2.9*	0.2
EA	wt.-%	46.34	4.1	0	14.03	--
	at.-%	3.86	4.07	0	0.44	--
	Normalized to 37 C atoms at.-%	37	39.01	0	4.20	--
EDX	at.-%	76.6	--	--	6.1	0.5
	Normalized to 37 C atoms at.-%	37	--	--	2.9	0.2
Titration	Normalized to 37 atoms at.-%	37	--	--	2.9	--

*The sulfur content was calculated from titration curve shown in Figure S3B.

Table S6. Composition calculated from EA, EDX, and titration normalized to 37 C atoms corresponding to the repeating unit of SPAF-2_{0.8}.

SPAF-2_{0.8}		C	H	N	S	Br
Composition	at.-%	37	33.1	--	4.8*	0.2
EA	wt.-%	47.35	3.55	0.11	15.29	--
	at.-%	3.94	3.52	0.01	0.48	--
	Normalized to 37 C atoms at.-%	37	33.06	0.07	4.48	--
EDX	at.-%	78	--	--	9.8	0.5
	Normalized to 37 C atoms at.-%	37	--	--	4.6	0.2
Titration	Normalized to 37 atoms at.-%	37	--	--	4.8	--

*The sulfur content was calculated from titration curve displayed in Figure S3C.

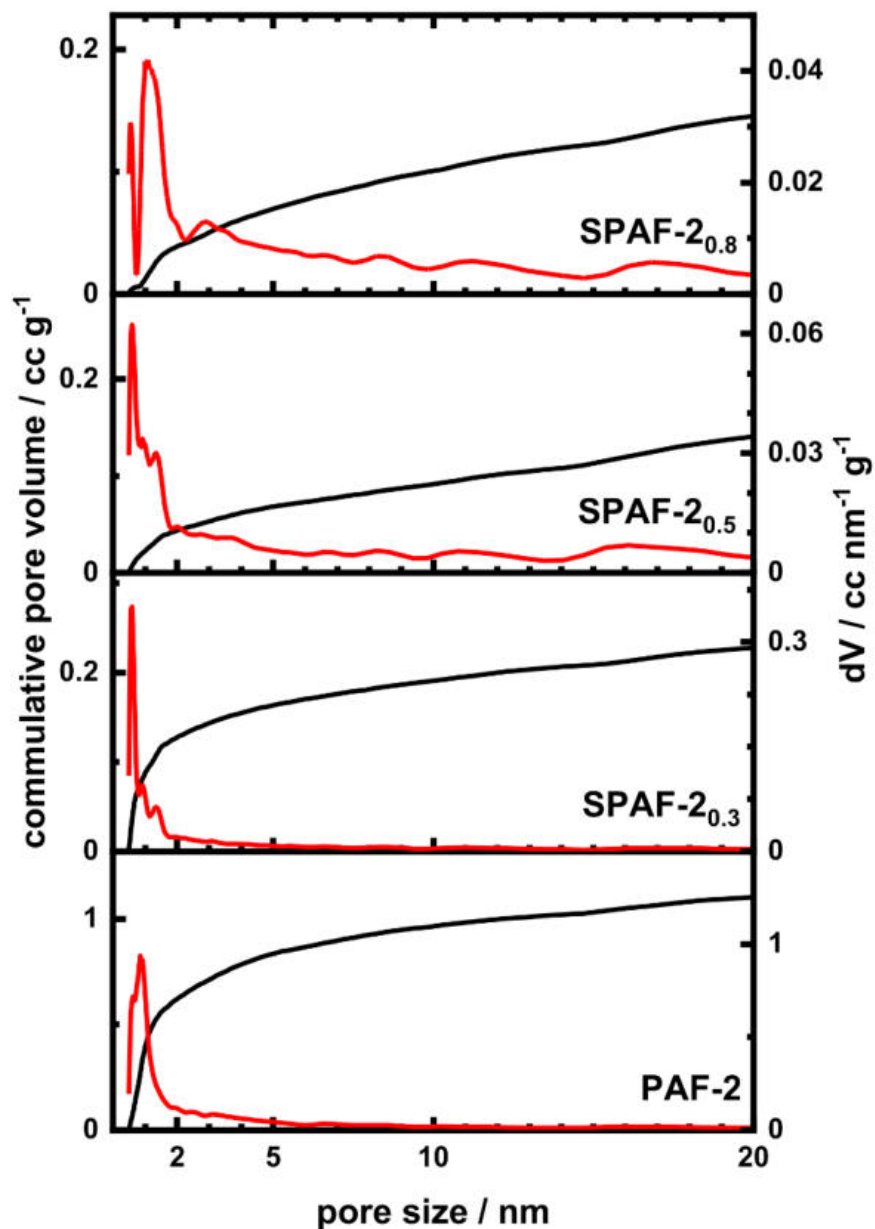


Figure S2. Calculated pore size distribution dV (red) and cumulative pore volume (black). The distributions and volumes were calculated from Ar adsorption branches (Figure S1B) with Ar at 87 K on carbon QSDFT (slit pore, QSDFT equilibrium model) kernel.

Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework

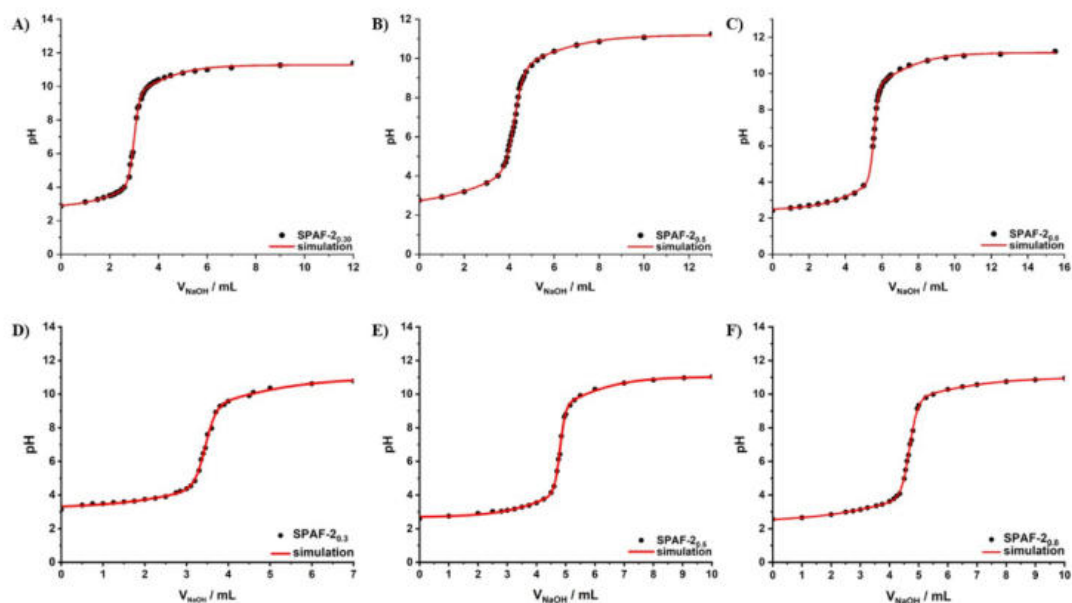


Figure S3. Titration curve of SPAF-2_{0.3} (A, D), SPAF-2_{0.5} (B, E), and SPAF-2_{0.8} (C, F) with 10 mM NaOH. A-C are after synthesis and D-F after temperature dependent EIS and NMR spectroscopic measurements to verify the long-term stability of the sulfonated frameworks.

Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework

Table S7. Titration of SPAF-2 derivatives to determine the sulfonation degree x after washing.

		M_{SPAF-2} / mg	V_{NaOH} / ml*	x / %	IEC / mequiv g⁻¹
SPAF-2 _{0.3}	as synthesized	10.7	2.967	29	2.77
	after EIS and NMR spectroscopy	11.9	3.452	30	2.90
SPAF-2 _{0.5}	as synthesized	10.3	4.242	50	4.12
	after EIS and NMR spectroscopy	11.7	4.825	49	4.12
SPAF-2 _{0.8}	as synthesized	10.0	5.630	80	5.63
	after EIS and NMR spectroscopy	8.5	4.700	78	5.53

*V_{NaOH} determined from fitting the 1st derivation of the titration curves (Figure S3).

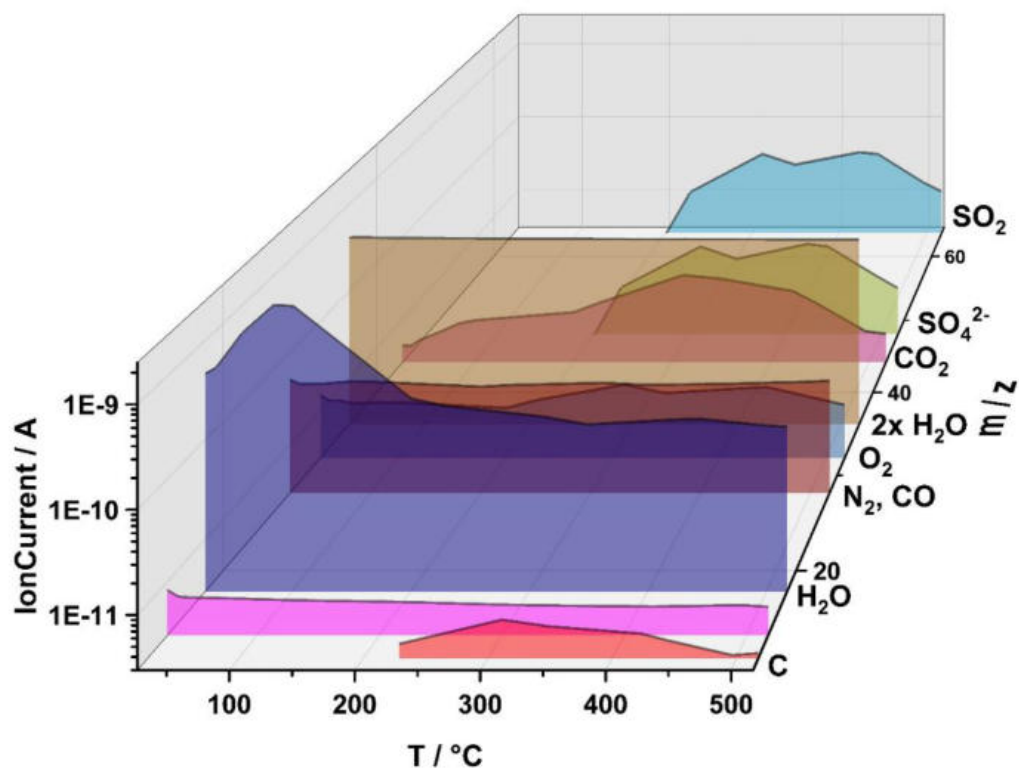


Figure S4. Thermal gravimetric analysis with detection of the decomposition gases via mass spectrometry of SPAF-2_{0.5}.

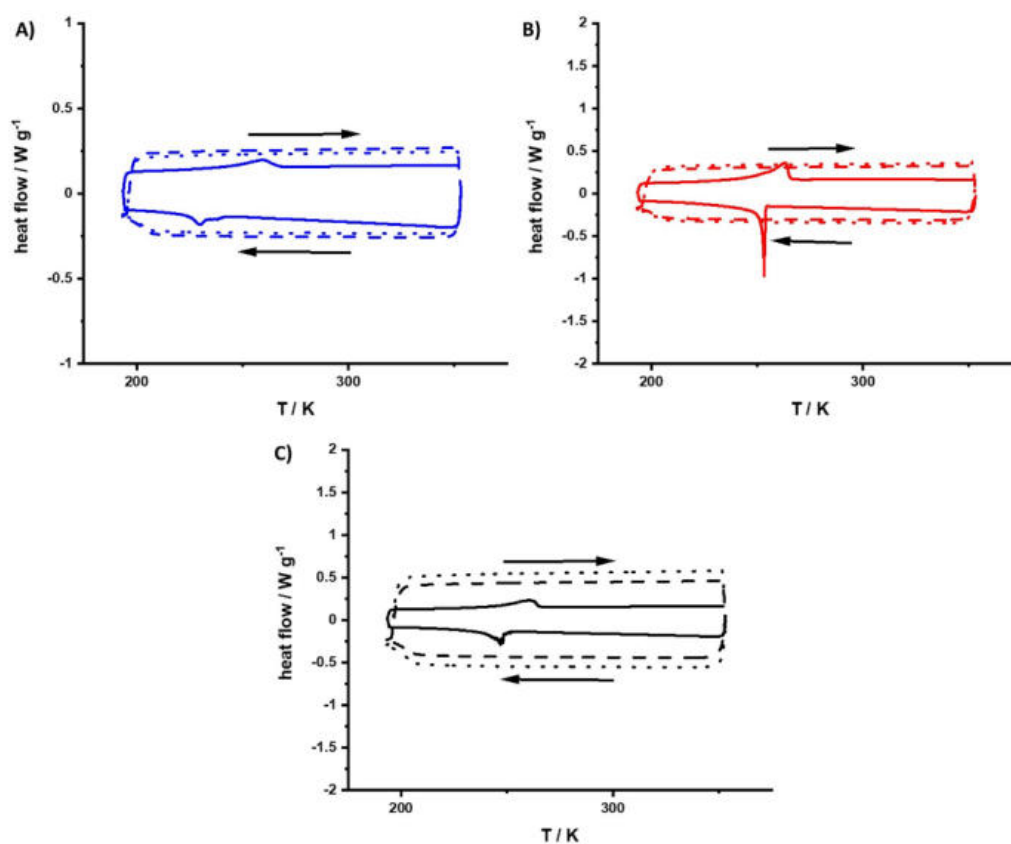


Figure S5. Differential scanning calorimetry measurements of SPAF-20.3 (A), SPAF-20.5 (B), and SPAF-20.8 (C) at 33 % RH (dotted), 67 % RH (dashed), and 100 % RH (solid).

Table S8. Melting enthalpies and melting temperatures (onset and peak) of $SPAF-2_x^{RH}$. The melting enthalpy of bulk ice for calculating the amount of mesopore water is 333.55 J g^{-1} . The total amount of adsorbed water was derived from the water isotherms (Figure 1).

	33 % RH		67 % RH		100 % RH		Proportion Mesopore Water %
	$T_{on}/T_p / \text{K}$	$\Delta H_m / \text{J g}^{-1}$	$T_{on}/T_p / \text{K}$	$\Delta H_m / \text{J g}^{-1}$	$T_{on}/T_p / \text{K}$	$\Delta H_m / \text{J g}^{-1}$	
SPAF-2 _{0.3}	--	--	--	--	242.5/259.6	7.8	4.9
SPAF-2 _{0.5}	--	--	--	--	251.3/263.3	21.9	14.3
SPAF-2 _{0.8}	--	--	--	--	246.2/260.6	11.0	7.8

Electrochemical impedance spectroscopy

Choice of the equivalence circuits for the refinements of the EI spectra

The pore sizes of SPAF-2_x are pretty narrow (roughly 1 nm), which strongly influences the frequency-dependent impedance. In particular, small displacements between the negatively charged sulfonate groups attached to the framework racks and the mobile oxonium ions in the aqueous phase lead to local polarization, inducing a capacitance (Figures S6C, S6D). In this respect, SPAF-2_x^{RH} resembles more a defect-driven ionic conductivity in solid electrolytes¹² than the one found for electrolyte host systems with larger micropores and mesopores or fluid electrolytes. The impedance spectra for the latter systems are often described with equivalence circuits that include Randles-like elements. An ohmic resistor then treats the ionic conductivity.

Due to the local polarization (Figures S6C and S6D), instead, we use an RC element for determining the ionic bulk resistance of the adsorbed electrolyte for all spectra. This effect is evident for frameworks that were only partially filled with water by equilibration at 33 % RH and 67 % RH. Figure 2 and S6A show an example spectrum collected for SPAF-2_{0.5}³³ at room temperature. The Nyquist plot exhibits three nicely resolved half circuits refined with three RC elements (Figure S6C) supported by the corresponding distribution of relaxation time (DRT) analysis leading to three well-resolved peaks (Figure S6B). For the first relaxation process ($\tau \approx 10^{-6}$ s), the capacity is on the order of 10^{-12} F, which is typical for the polarization of the micropores. The second relaxation process ($\tau \approx 10^{-3}$ s) describes the grain boundaries with a 10^{-7} F capacity. The third circuit, with a capacity of $\approx 10^{-4}$ F and a relaxation time $\tau \approx 10^{-1}$ s, is typical for polarization and chemical reactions at the copper electrodes.^{12,13} The latter parameters are characteristic of the sample setup based on two cylindrical electrodes squeezing a preprepared and water-equilibrated sample pellet with the same diameter (Figure S6C). As the ohmic resistances are high, small contributions of electrodes and cables become negligible, and an equivalence circuit with three RC elements is sufficient for the refinements.

In contrast, the ionic resistances are significantly smaller for frameworks equilibrated at 100 % RH (SPAF-2_x¹⁰⁰), reaching similar values to the sample setup. Shortcut measurements in moist environments at room temperature revealed inductive and ohmic contributions for the latter. The short-cut spectra could best be refined by a parallel arrangement of a coil with an inductance of about 10^{-6} H and a resistor with a resistance of several hundred Ohm. Thus, we added a similar element (grey box) to the equivalence circuit for refining the EIS measurements for SPAF-2_x¹⁰⁰ (Figures 2B and S6D). Similar values as for the short-cut were observed (Tables S12, S13, S16–S21). The inductances varied between $1.2 \cdot 10^{-7}$ and $1.1 \cdot 10^{-6}$ H and were almost temperature-independent. For the parallel resistor (R_E), values between 50 and 350 Ω were found with no clear temperature dependence, sometimes rising and sometimes falling with increasing temperature. In one case, even an infinite resistance was observed. We attribute this to a roughness of the pellet and electrode surfaces, leading to slightly varying contacts for each sample and temperature. However, these trends and the shortcut measurements clearly show that this element does not represent the sample impedances.

Figure S6F shows, exemplary, the DRT analysis of the EIS spectrum SPAF-2_{0.8}¹⁰⁰ (Figure S6E). Three relaxation processes can be distinguished. The one with the highest relaxation time is typical for polarization and chemical reactions at the copper electrodes and exhibits a similar relaxation time $\tau \approx 10^{-1}$ s as observed for the partially water-filled frameworks (Figures S6B and S6F). One RC element (marked with EI) is introduced to the corresponding equivalence circuit (Figure S6D). The electrodes and cables cause the relaxation process with the shortest relaxation time $\tau \approx 5 \cdot 10^{-6}$ s. It is represented by a coil and, in parallel, a resistor (marked with E) in an equivalence circuit. This leaves one relaxation process at $\tau \approx 5 \cdot 10^{-6}$, for which one additional RC element (marked with B/GB) is added to the equivalence circuit (Figures 2B and S6D). As explained above, polarization effects due to relative displacements of the oxonium ions and the sulfonate groups are expected in the micropores and grain boundaries. Consequently, this remaining RC element accounts for the charge transport within the micropores and over the grain boundaries, demonstrating that the charge transport is similar for both processes.

This can be explained when considering that for equilibration in 100% RH, the samples also adsorb water at the grain surfaces, forming a thin water layer through which the oxonium ions diffuse unhindered. The ¹H SFG NMR spectroscopic experiments demonstrating that water molecules and oxonium ions diffuse almost as fast as bulk water on length scales of a few hundred nanometers support this finding. If a water layer forms between the grains in a pressed pellet, an additional layer is expected to form between the surfaces of the pellet and the electrodes (Figure S6D). This layer will behave like a liquid electrolyte and can thus be treated with an ohmic resistance (R_{WL}), as shown in Figures 2B and S6D. As for the electrode/cable element, the resistance will depend on the layer thickness and the surface roughness of the electrodes and the pellets.

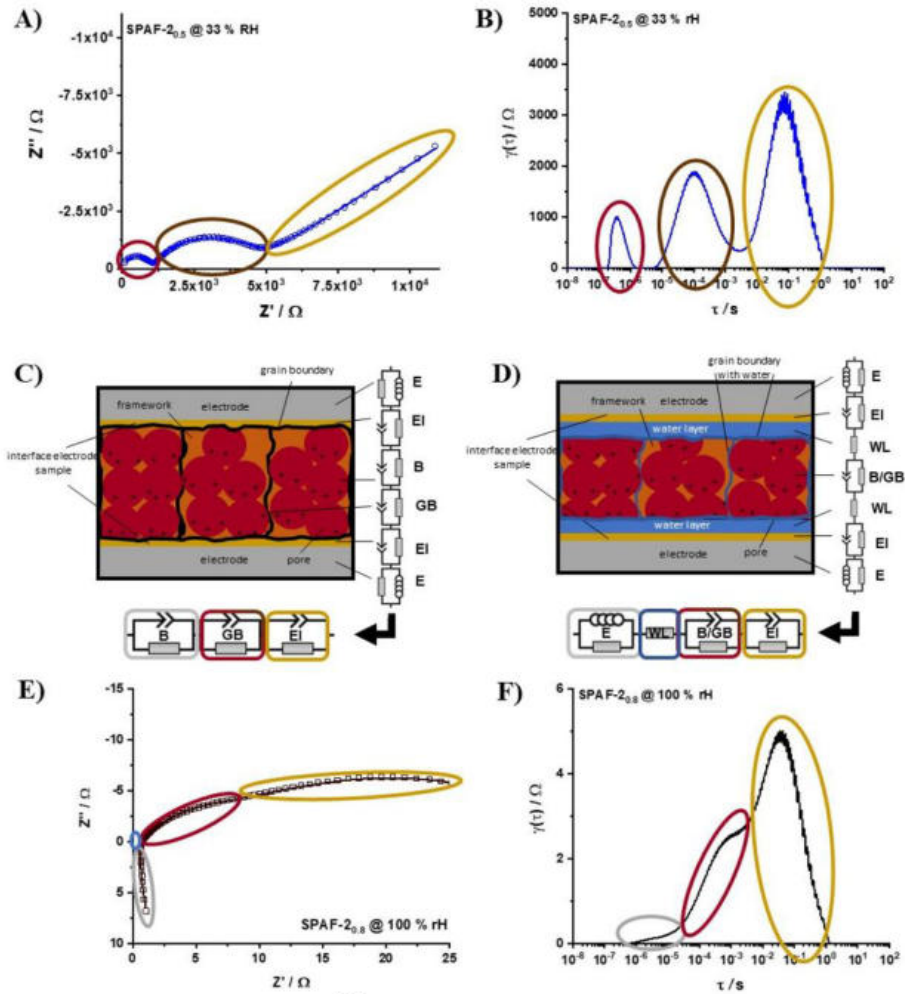


Figure S6. A) Nyquist plot of SPAF-2_{0.5}³³ at 300 K. B) Distribution of relaxation times, calculated from EI spectrum shown in A). C) Schematic sample setup highlighting the relaxation processes and their elements in the equivalence circuits for samples with $x < 0.8$ and RH < 100 % RH. RC elements for bulk (B), the grain boundaries (GB) and the electrode interface (EI) were used. The elements are marked with colored boxes and the same color code is used for assigning the corresponding relaxation processes to the Nyquist plot and the DRT analysis in A) and B). D) Schematic sample setup highlighting the relaxation processes and their elements in the equivalence circuits for samples $x = 0.8$ or 100 % RH. Due to thin water layers between the grains the bulk and grain boundary relaxation merges into one RC element (B/GB). Additional water films between the pellets and the electrodes are represented by an ohmic resistor (R_{WL}). Furthermore, an element (E) representing influences of the electrodes and cables and an RC element for the electrode interface (EI) were added to the equivalence circuit (see above). The elements are marked with colored boxes and the same color code is used for assigning the corresponding relaxation processes to the Nyquist plot and the DRT analysis in E) and F). E) Impedance spectrum of SPAF-2_{0.8}¹⁰⁰ at 303 K. F) Distribution of relaxation times (DRT) of measurement in E).

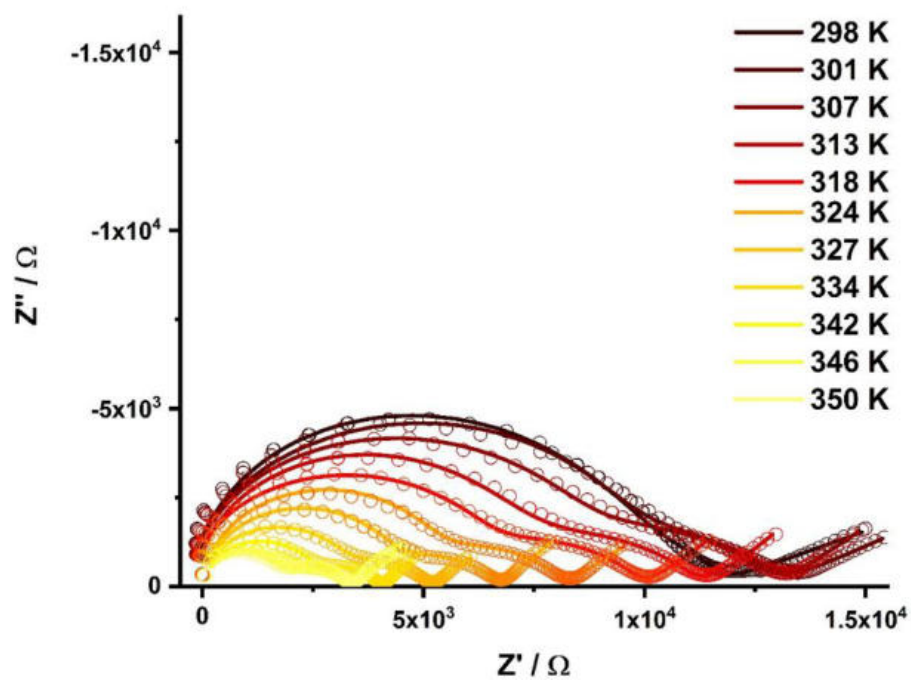


Figure S7. Nyquist plot of PAF-2 at 100 % RH.

Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like Micropores of a Sulfonated, Aromatic Framework

Table S9. Simulation parameters of the impedance measurements of PAF-2 at 100 % RH. The equivalent circuit shown in Figure 2A was used and a sample thickness is 0.11 cm.

T / K	bulk			grain boundaries			electrode interface		
	R _B / kΩ	CPE _B / 10 ⁻¹¹ S	α _B	R _{GB} / kΩ	CPE _{GB} / 10 ⁻⁷ S	α _{GB}	R _{EI} / Ω	CPE _{EI} / 10 ⁻⁴ S	α _{EI}
293	9.31 (41)	4.80(84)	1.00(1)	2.27(50)	1.34(74)	0.69(8)	1E15 (0)	1.96(5)	0.28(2)
299	8.86 (36)	4.93(89)	1.00(1)	4.02(46)	1.51(47)	0.65(4)	1E15 (0)	2.45(8)	0.31(2)
303	7.92 (26)	5.22(84)	1.00(1)	4.90(32)	1.43(28)	0.64(3)	1E15 (0)	2.47(8)	0.40(2)
307	6.82 (24)	5.54(94)	1.00(1)	4.32(29)	1.39(27)	0.65(3)	1E15 (0)	2.70(8)	0.41(2)
310	6.00 (18)	5.38(86)	1.00(1)	3.85(22)	1.40(27)	0.66(3)	1E15 (0)	3.09(10)	0.42(2)
318	4.90 (16)	5.70(97)	1.00(1)	3.25(19)	1.47(30)	0.66(3)	1E15 (0)	3.38(11)	0.44(2)
322	3.99 (13)	5.88(107)	1.00(1)	2.70(16)	2.12(49)	0.64(3)	1E15 (0)	3.16(10)	0.51(2)
329	2.96 (8)	6.14(104)	1.00(1)	2.16(10)	1.55(25)	0.66(2)	1E15 (0)	4.71(12)	0.46(2)
333	2.27 (6)	6.44(115)	1.00(1)	1.76(7)	2.11(32)	0.65(2)	1E15 (0)	4.68(11)	0.53(1)
340	1.86 (4)	6.67(122)	1.00(1)	1.45(5)	0.94(16)	0.72(2)	1E15 (0)	3.51(6)	0.50(1)
343	1.72 (5)	7.00(155)	1.00(1)	1.62(5)	1.10(21)	0.71(2)	1E15 (0)	3.59(6)	0.48(1)

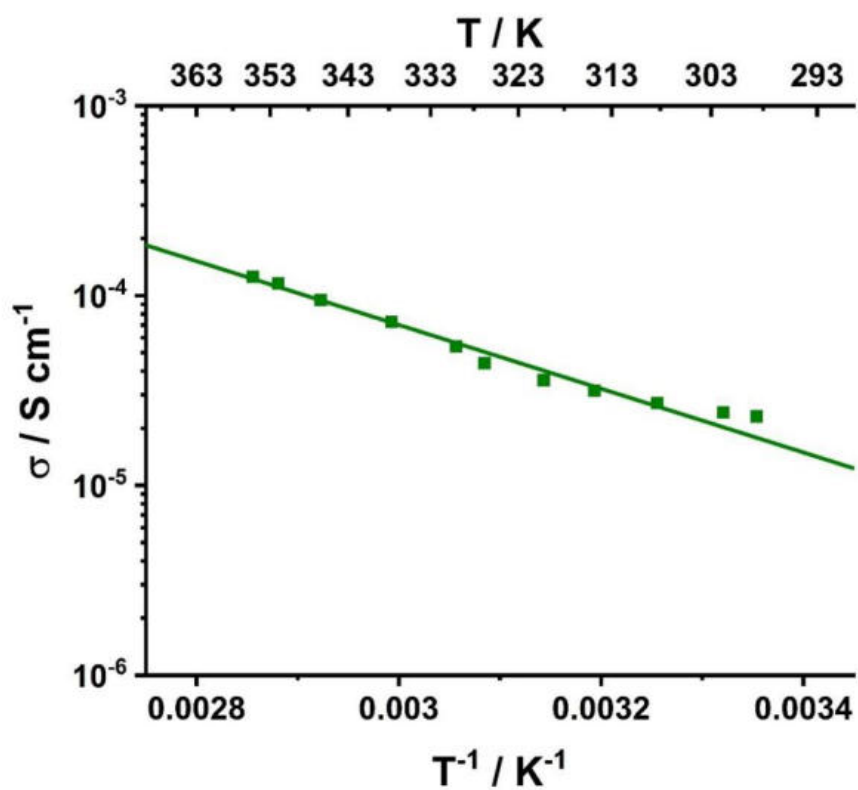


Figure S8. Arrhenius plot of the conductivity of PAF-2.

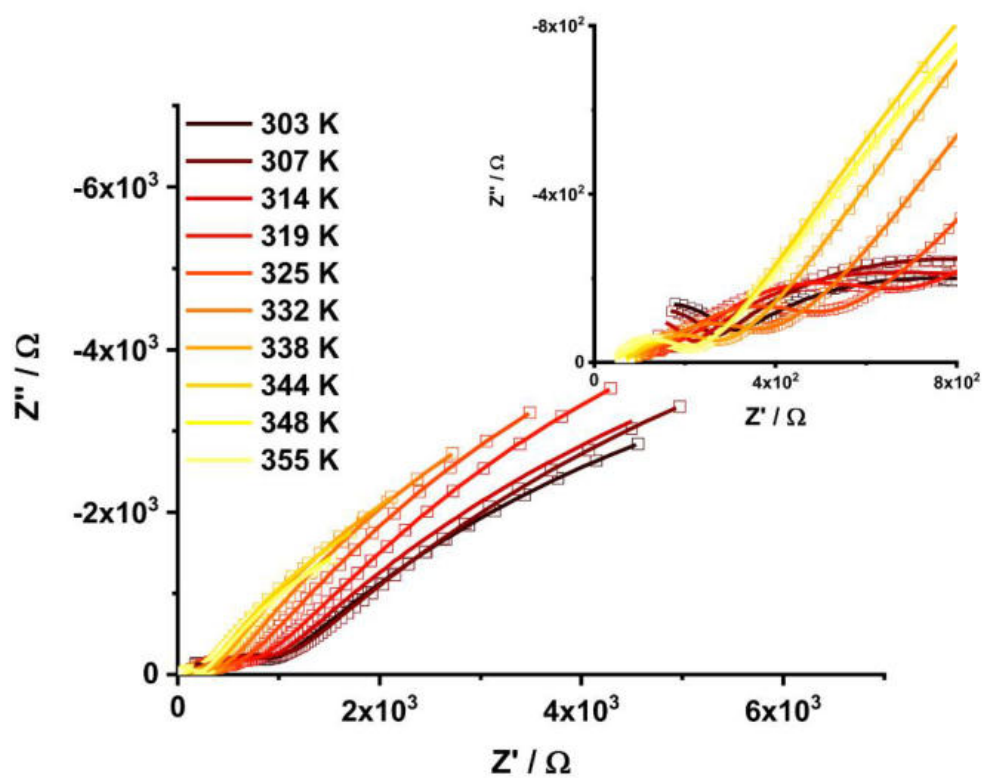


Figure S9. Nyquist plot of SPAF-2³³_{0.3}. The enlarged image section shows the bulk conductivity.

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Table S10. Simulation parameters of the impedance measurements of SPAF-2_{0.3}³³. The equivalent circuit shown in Figure 2A was used and the sample thickness is 0.03 cm.

T / K	bulk			grain boundaries			electrode interface		
	R _B / Ω	CPE _B / 10 ⁻⁷ S	α _B	R _{GB} / Ω	CPE _{GB} / 10 ⁻⁵ S	α _{GB}	R _{EI} / Ω	CPE _{EI} / 10 ⁻⁴ S	α _{EI}
298	212(12)	0.0011(5)	1.00(3)	230 (41)	23.06 (9.36)	0.30(5)	3386	1.46(2)	0.59(1)
303	269(2)	0.0027(5)	0.95(1)	706 (5)	0.33(1)	0.56(0)	15881	0.61(0)	0.57(0)
307	240(2)	0.0017(5)	0.98(1)	810 (6)	0.25(1)	0.59(0)	20135	0.56(0)	0.57(0)
314	195(2)	0.0011(5)	1.00(3)	706 (6)	0.27(1)	0.70(0)	18806	0.59(0)	0.58(0)
319	238(8)	3.02(48)	0.89(2)	15925 (362)	5.51(3)	0.70(0)	1E15	6.03(19)	0.15(0)
325	169(5)	2.86(43)	0.89(1)	15963 (279)	6.11(3)	0.71(0)	9.97E14	8.39(19)	0.14(0)
332	121(3)	2.78(37)	0.89(1)	14237 (189)	7.24(3)	0.72(0)	4.47E14	12.3(2)	0.13(0)
338	89(2)	2.53(33)	0.89(1)	11422 (121)	8.89(3)	0.72(0)	9.32E12	17.8(3)	0.13(0)
344	70(1)	2.33(30)	0.89(1)	8850 (81)	10.09(3)	0.72(0)	1.45E13	24.8(3)	0.11(0)
348	75(1)	1.16(17)	0.92(1)	6581 (87)	12.93(6)	0.73(0)	1.43E10	21.8(3)	0.12(0)
355	85(1)	1.11(14)	0.91(1)	6335 (85)	13.94(6)	0.73(0)	5.54E13	22.3(3)	0.13(0)

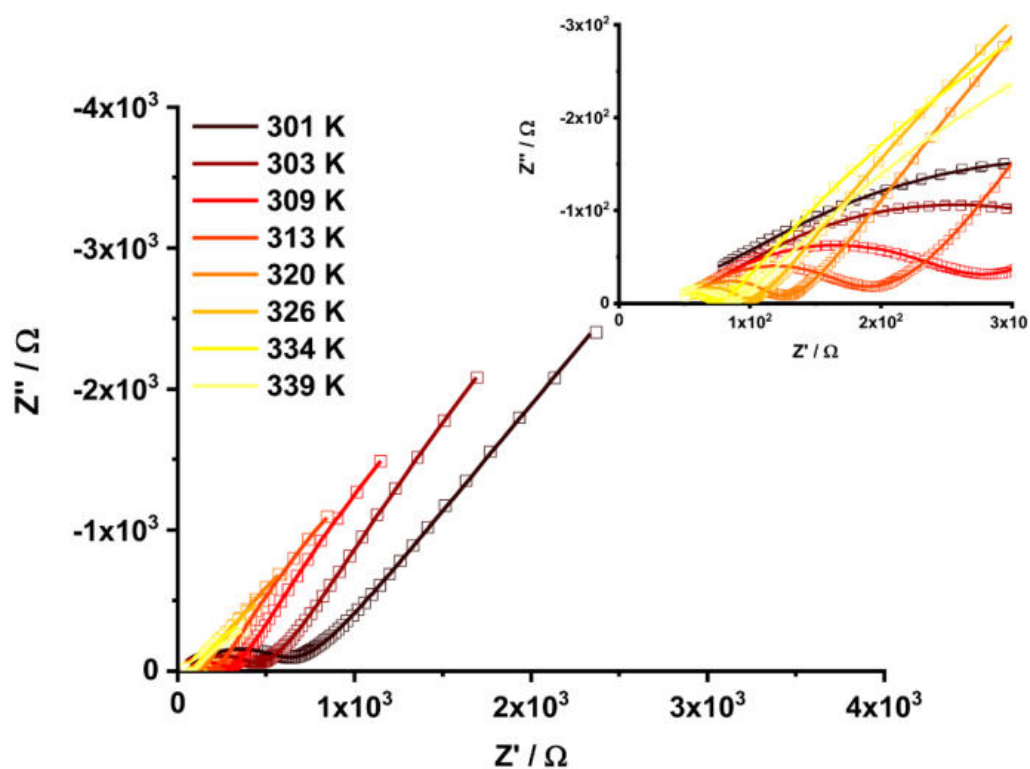


Figure S10. Nyquist plot of SPAF-2_{0.3}⁶⁷. The enlarged image section shows the bulk conductivity.

Table S11. Simulation parameters of the impedance measurements of SPAF-2_{0.3}⁶⁷. The equivalent circuit shown in Figure 2A was used and the sample thickness is 0.08 cm.

T / K	bulk			grain boundaries			electrode interface		
	R _B / Ω	CPE _B / 10^{-7} S	α_B	R _{GB} / Ω	CPE _{GB} / 10^{-4} S	α_{GB}	R _{EI} / k Ω	CPE _{EI} / 10^{-4} S	α_{EI}
301	371 (8)	3.81 (19)	0.69 (1)	583 (18)	2.54(29)	0.23 (1)	129(54)	1.07(1)	0.65 (0)
303	265 (2)	3.70 (13)	0.71 (0)	26530 (3062)	1.08(1)	0.77 (0)	7.06E9(0)	16.2(2)	0.13 (0)
309	148 (1)	2.76 (11)	0.74 (0)	15810 (1156)	1.45(1)	0.77 (0)	1.21E10	28.3(4)	0.10 (0)
313	88 (1)	1.66(8)	0.78 (0)	10398 (610)	1.95(2)	0.76 (0)	3.99E5	42.8(2.0)	0.08 (0)
320	47 (2)	0.62(8)	0.84 (1)	270 (131)	42.7 (15.7)	0.07 (1)	6.14(41)	3.13(3)	0.73 (0)
326	30 (1)	0.35(6)	0.89 (1)	136 (25)	30.8 (116)	0.08 (2)	3.97(23)	4.41(5)	0.71 (0)
334	12 (1)	0.11(4)	1.00 (3)	75 (1)	3.04(98)	0.19 (2)	2.38(12)	6.62(8)	0.67 (0)
339	28 (2)	0.66 (19)	0.86 (2)	1855 (619)	112.9 (1723)	0.04 (4)	1.58(11)	6.71(13)	0.66 (1)

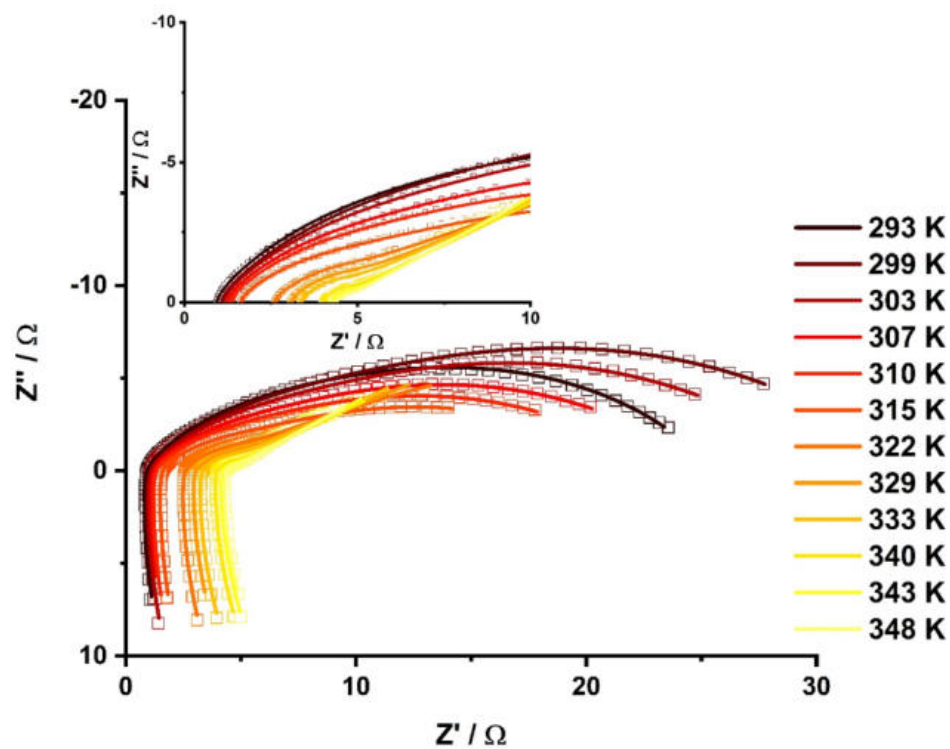


Figure S11. Nyquist plot of SPAF-2¹⁰⁰_{0.3}.

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Table S12. Simulation parameters of the impedance measurements of SPAF-2_{0.3}¹⁰⁰. The equivalent circuit shown in Figure 2B was used and the sample thickness is 0.14 cm.

T / K	electrode			bulk/grain boundaries			electrode interface		
	R _{WL} / Ω	R _E / Ω	L / 10^{-6} H	R _{B/GB} / Ω	CPE _{B/GB} / 10^{-3} S	$\alpha_{B/GB}$	R _{EI} / Ω	CPE _{EI} / 10^{-3} S	α_{EI}
293	0.71 (1)	128 (10)	1.08(0)	3.76(80)	1.39(5)	0.64(1)	18.0(8)	3.41(16)	0.61 (1)
299	0.80 (1)	111 (7)	1.08(0)	5.37(1.04)	1.59(8)	0.64(1)	27.6(8)	4.84(12)	0.53 (1)
303	0.85 (1)	119 (7)	1.09(0)	4.62(1.40)	1.68(17)	0.66(3)	25.8(9)	5.11(16)	0.52 (1)
307	0.97 (1)	106 (6)	1.07(0)	3.59(1.30)	1.94(19)	0.68(2)	21.6(5)	6.47(12)	0.50 (1)
310	1.07 (1)	116 (8)	1.07(0)	3.03(1.09)	2.34(36)	0.69(4)	19.8(6)	8.53(23)	0.48 (1)
318	1.38 (2)	112 (9)	1.07(0)	2.32(70)	4.13(70)	0.64(4)	18.6(10)	1.89(69)	0.44 (2)
322	2.34 (3)	90 (7)	1.07(0)	1.58(35)	3.28(107)	0.72(6)	40.7(40)	36.51 (1.09)	0.38 (2)
329	2.80 (3)	78 (8)	1.05(0)	1.15(27)	2.83(126)	0.76(8)	81.2 (223)	47.93 (199)	0.36 (2)
333	3.08 (4)	76 (6)	1.06(0)	0.82(21)	1.97(131)	0.84 (11)	1100	60.18 (2.93)	0.34 (2)
340	3.78 (2)	72 (5)	1.05(0)	0.71(18)	0.88(83)	0.95 (12)	3.0E12	72.62(62)	0.35 (1)
343	4.08 (2)	70 (6)	1.05(0)	0.64(17)	1.56(203)	0.87 (16)	1.1E14	71.94(76)	0.37 (1)
348	4.20 (1)	66 (6)	1.03(0)	0.48(17)	1.49(254)	0.89 (20)	1E15	82.64(93)	0.37 (1)

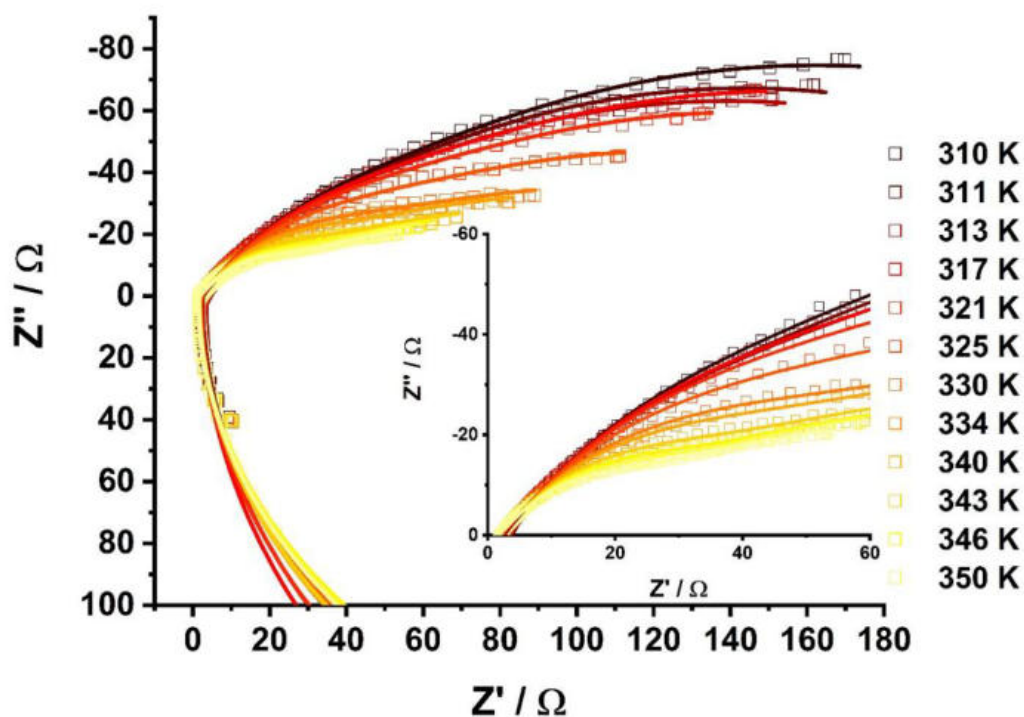


Figure S12. Nyquist plot of SPAF-2_{0.3} after water immersion. The enlarged image section shows the bulk conductivity and the results for simulations with the equivalent circuit shown in Figure 2B are given in Table S13.

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Table S13. Simulation parameters of the impedance measurements of SPAF-2_{0.3} after water immersion. The equivalent circuit shown in Figure 2B was used and the sample thickness is 0.21cm.

T / K	electrode			bulk/grain boundaries			electrode interface		
	R _{WL} / Ω	R _E / Ω	L / 10 ⁻⁶ H	R _{B/GB} / Ω	CPE _{B/GB} / 10 ⁻⁶ S	$\alpha_{B/GB}$	R _{EI} / Ω	CPE _{EI} / 10 ⁻⁵ S	α_{EI}
310	2.45 (2)	348 (41)	1.13(7)	20.7(64)	650(119)	0.82(5)	286(8)	106(9)	0.60(1)
311	2.44 (2)	348 (43)	1.14(7)	14.9(48)	612(148)	0.86(6)	258(6)	101(7)	0.61(1)
313	2.27 (7)	387 (54)	1.14(7)	18.8(67)	711(139)	0.83(6)	245(7)	119(12)	0.60(1)
317	2.11 (2)	429 (69)	1.14(7)	26.7(94)	759(110)	0.81(5)	262(11)	148(21)	0.58(1)
321	2.00 (2)	383 (57)	1.13(7)	27.7(95)	769(104)	0.80(5)	240(12)	176(28)	0.57(1)
326	1.85 (2)	329 (45)	1.13(8)	28.9(91)	751(94)	0.80(5)	196(14)	243(49)	0.55(1)
330	1.72 (2)	341 (50)	1.13(8)	29.5(79)	750(84)	0.79(4)	157(19)	381(96)	0.51(2)
334	1.69 (2)	340 (49)	1.13(8)	24.7(61)	745(93)	0.81(4)	148(16)	390(84)	0.51(1)
340	1.59 (2)	335 (50)	1.13(8)	19.5(44)	766(110)	0.82(4)	132(16)	484(95)	0.50(1)
343	1.54 (2)	302 (43)	1.13(9)	17.2(37)	788(123)	0.83(4)	127(18)	558(106)	0.49(1)
346	1.52 (2)	311 (46)	1.13(9)	15.4(31)	793(130)	0.84(4)	128(18)	589(102)	0.48(1)
350	1.50 (2)	315 (46)	1.13(9)	13.1(26)	810(142)	0.85(4)	112(15)	629(103)	0.48(1)

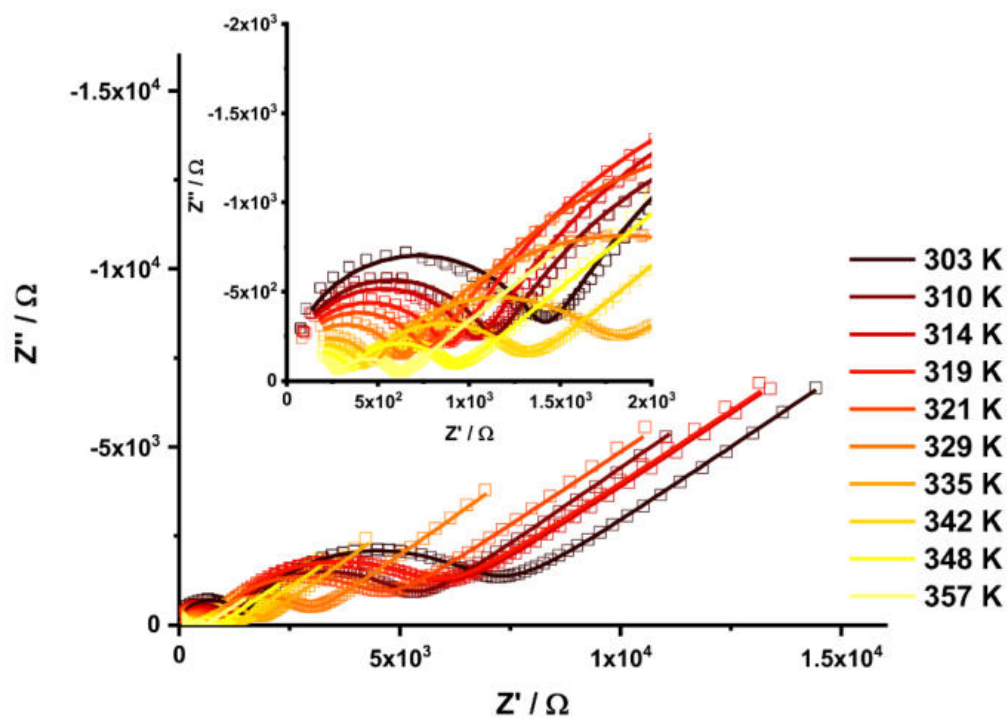


Figure S13. Nyquist plot of SPAF-2³³_{0.5}. The enlarged image section shows the bulk conductivity.

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Table S14. Simulation parameters of the impedance measurements of SPAF-2_{0.5}³³. The equivalent circuit shown in Figure 2B was used and the sample thickness is 0.06 cm.

T / K	bulk			grain boundaries			electrode interface		
	R _B / Ω	CPE _B / 10 ⁻¹⁰ S	α _B	R _{GB} / Ω	CPE _{GB} / 10 ⁻⁷ S	α _{GB}	R _{EI} / 10 ¹⁴ Ω	CPE _{EI} / 10 ⁻⁵ S	α _{EI}
303	1327 (8)	1.02 (1)	1.00 (1)	5246 (91)	1.54(7)	0.77 (1)	10.0	4.31(17)	0.44 (1)
310	1067 (6)	0.98 (10)	1.00 (1)	3814 (59)	7.62(8)	0.78 (1)	10.0	5.29(21)	0.45 (2)
314	968(6)	1.00 (10)	1.00 (1)	4349 (67)	1.57(7)	0.78 (1)	5.28	4.36(13)	0.44 (1)
319	820(6)	0.99(9)	1.00 (1)	4337 (50)	1.83(6)	0.77 (0)	3.98	4.33(9)	0.44 (1)
321	717(3)	0.99(9)	1.00 (1)	3419 (39)	2.06(7)	0.76 (0)	5.19	5.38(11)	0.44 (1)
329	592(2)	0.98(6)	1.00 (0)	2176 (13)	2.34(5)	0.75 (0)	4.39	7.71(11)	0.46 (1)
335	452(1)	0.98(6)	1.00 (0)	1262 (6)	2.01(5)	0.76 (0)	9.68	12.3(2)	0.46 (0)
342	389(1)	0.99 (7)	1.00 (0)	846 (5)	1.76(6)	0.78 (0)	9.45	17.2(3)	0.44 (0)
348	322(1)	1.00(8)	1.00 (0)	551 (3)	1.66(6)	0.78 (0)	8.87	24.4(4)	0.44 (0)
357	270(1)	1.00(7)	1.00 (0)	319 (2)	1.45(5)	0.79 (0)	4.13	37.6(5)	0.44 (0)

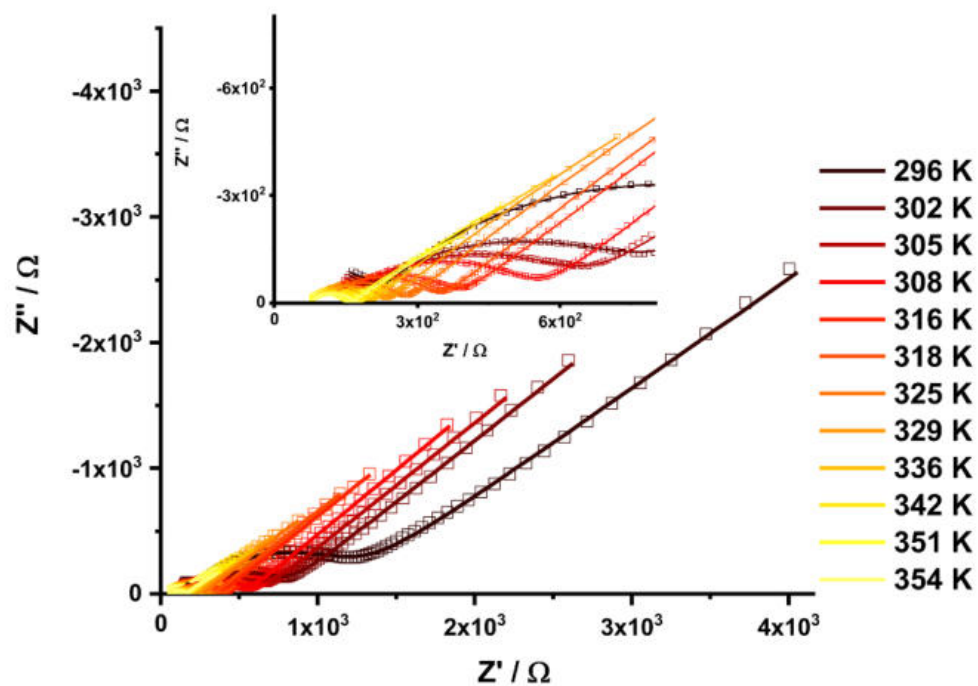


Figure S14. Nyquist plot of SPAF-2_{0.5}⁶⁷. The enlarged image section shows the bulk conductivity.

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Table S15. Simulation parameters of the impedance measurements of SPAF-2_{0.5}⁶⁷. The equivalent circuit shown in Figure 2A was used and the sample thickness is 0.06 cm.

T / K	bulk			grain boundaries			electrode interface		
	R _B / Ω	CPE _B / 10 ⁻¹¹ S	α _B	R _{GB} / Ω	CPE _{GB} / 10 ⁻⁷ S	α _{GB}	R _{EI} / kΩ	CPE _{EI} / 10 ⁻⁴ S	α _{EI}
296	207(3)	98.2 (511)	0.87 (3)	932 (6)	12.1(5)	0.66 (0)	1E12 (0)	1.11(0)	0.46 (0)
302	172(2)	10.2 (4.7)	1.00 (3)	590 (4)	19.0(7)	0.61 (0)	1E12 (0)	1.54(0)	0.49 (0)
305	159(2)	9.84 (579)	1.00 (4)	479 (4)	17.3(9)	0.61 (0)	9.65E11 (0)	1.80(0)	0.50 (0)
308	145(1)	8.92 (395)	1.00 (3)	397 (2)	10.2(3)	0.63 (0)	6.47E11 (0)	2.11(0)	0.51 (0)
316	117(1)	7.89 (382)	1.00 (3)	259 (1)	7.78(22)	0.66 (0)	7.90E9 (0)	2.97(0)	0.50 (0)
318	105(1)	7.14 (3.84)	1.00 (3)	233 (1)	5.55(15)	0.68 (0)	82.9 (13.6)	3.46(1)	0.50 (0)
325	87.6(7)	5.45 (453)	1.00 (5)	181 (1)	4.75(12)	0.69 (0)	15.8(6)	4.45(1)	0.51 (0)
329	80.2(6)	4.56 (416)	1.00 (5)	150 (1)	4.19(9)	0.70 (0)	8.61(19)	5.41(1)	0.52 (0)
342	73.0(6)	3.39 (500)	1.00 (9)	125 (1)	4.57(11)	0.70 (0)	4.38(7)	6.60(2)	0.52 (0)
351	72.9(6)	3.53 (462)	1.00 (8)	103 (1)	4.23(11)	0.70 (0)	3.50(6)	8.68(2)	0.52 (0)
354	70.6 (11)	2.88 (878)	1.00 (17)	84.6 (12)	4.71(24)	0.70 (1)	1.90(6)	11.8(8)	0.50 (0)

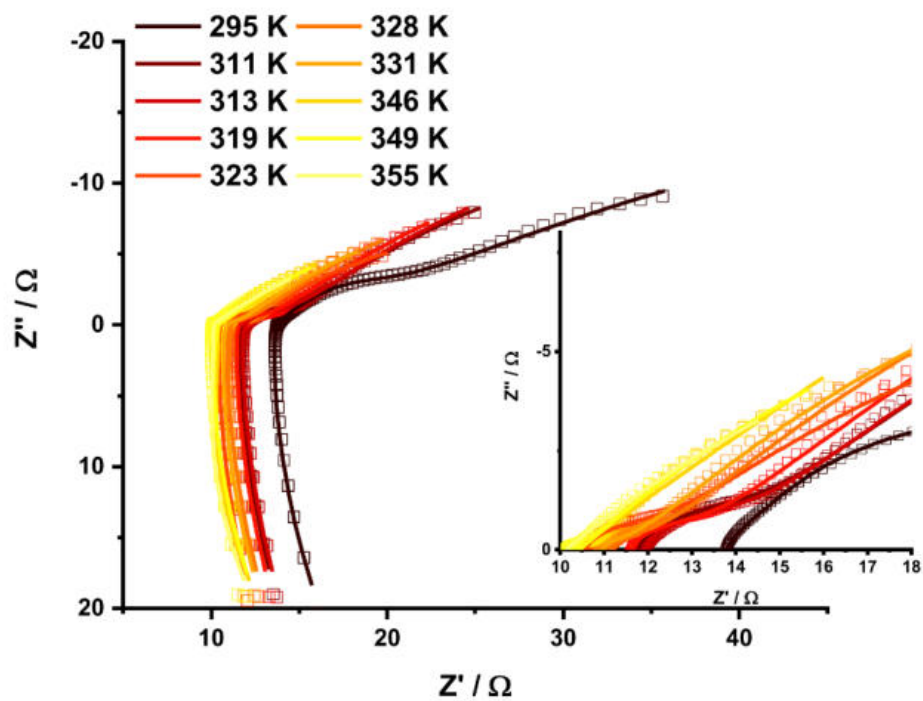


Figure S15. Nyquist plot of SPAF-2¹⁰⁰_{0.5}. The enlarged image section shows the bulk conductivity.

Table S16. Simulation parameters of the impedance measurements of SPAF-2¹⁰⁰_{0.5}. The equivalent circuit shown in Figure 2B was used and the sample thickness is 0.26 cm.

T / K	electrode			bulk/grain boundaries			electrode interface		
	R _{WL} / Ω	R _E / Ω	L / 10^{-7} H	R _{B/GB} / Ω	CPE _{B/GB} / 10^{-3} S	$\alpha_{B/GB}$	R _{EI} / Ω	CPE _{EI} / 10^{-2} S	α_{EI}
295	13.4 (2)	145(7)	7.09(2)	3.68(25)	0.98(13)	0.76(2)	105(8)	2.00(4)	0.37(1)
311	11.6 (0)	178(13)	6.61(2)	2.58(22)	2.61(48)	0.58(2)	58.3(73)	2.28(11)	0.52(2)
313	11.8 (0)	179(14)	6.66(2)	2.20(21)	2.47(56)	0.60(3)	74.8(137)	2.53(13)	0.50(2)
319	11.4 (0)	183(15)	6.66(2)	1.69(18)	2.72(78)	0.60(3)	67.4(131)	2.92(15)	0.50(2)
323	10.4 (0)	209(22)	6.60(2)	1.66(19)	2.64(53)	0.61(2)	32.0(29)	3.24(13)	0.61(2)
328	10.9 (0)	184(15)	6.76(3)	1.32(19)	5.41(26)	0.53(5)	41.3(7.1)	3.19(20)	0.54(2)
331	10.7 (0)	180(14)	6.76(3)	1.10(19)	7.31(432)	0.50(6)	33.3(55)	3.53(23)	0.54(2)
346	10.2 (0)	190(13)	6.64(2)	0.66(9)	9.56(566)	0.49(6)	22.1(17)	3.40(15)	0.58(1)
349	10.1 (0)	171(11)	6.67(2)	0.64(13)	1.89(141)	0.41(8)	21.0(17)	4.18(16)	0.58(2)
355	9.94 (2)	187(10)	6.55(1)	0.43(5)	9.65(522)	0.50(5)	16.1(8)	0.97(52)	0.50(5)

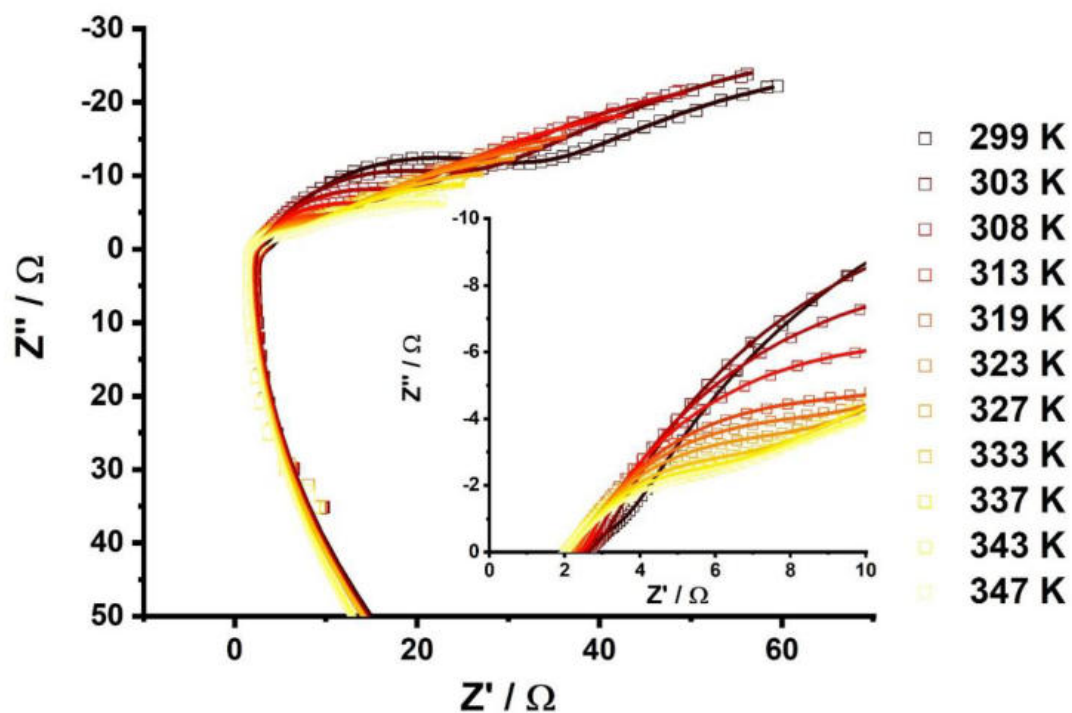


Figure S16. Nyquist plot of SPAF-2_{0.5} after water immersion. The enlarged image section shows the bulk conductivity and the results for simulations with the equivalent circuit shown in Figure 2B are given in Table S17.

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Table S17. Simulation parameters of the impedance measurements of SPAF-2_{0.5} after water immersion. The equivalent circuit shown in Figure 2B was used and the sample thickness is 0.29 cm.

T / K	electrode			bulk/grain boundaries			electrode interface		
	R_{WL} / Ω	R_E / Ω	$L / 10^{-6} \text{ H}$	$R_{B/GB} / 10^{-1} \Omega$	$CPE_{B/GB} / 10^{-6} \text{ S}$	$\alpha_{B/GB}$	R_{EI} / Ω	$CPE_{EI} / 10^{-4} \text{ S}$	α_{EI}
299	1.88(3)	225(16)	1.04(1)	154(6)	112(10)	0.98(2)	647(425)	106(68)	0.36(1)
303	2.11(3)	246(27)	1.02(1)	120(6)	101(13)	1.00(2)	257(55)	81.9(47)	0.41(1)
308	2.05(3)	250(28)	1.02(1)	84.9(43)	110(16)	1.00(2)	177(23)	81.8(38)	0.43(1)
313	1.93(3)	252(28)	1.02(1)	58.3(34)	123(22)	1.00(3)	154(18)	92.5(39)	0.43(1)
319	1.80(3)	249(26)	1.02(1)	36.9(26)	148(34)	1.00(3)	129(14)	107(41)	0.42(1)
323	1.74(3)	249(26)	1.02(1)	29.6(23)	162(44)	1.00(4)	120(12)	115(44)	0.41(1)
327	1.68(3)	239(23)	1.01(1)	22.8(21)	183(58)	1.00(4)	106(10)	126(47)	0.40(1)
333	1.58(3)	243(24)	1.02(1)	15.6(19)	228(96)	1.00(6)	86.2(77)	141(54)	0.39(1)
337	1.48(3)	263(27)	1.02(1)	11.7(18)	292(154)	1.00(7)	81.3(76)	157(64)	0.37(1)
343	1.42(3)	249(22)	1.01(1)	8.40(17)	350(237)	1.00(9)	49.5(2.8)	150(66)	0.36(1)
347	1.42(2)	256(21)	1.02(1)	8.14(16)	358(239)	1.00(9)	47.3(2.3)	142(61)	0.36(1)

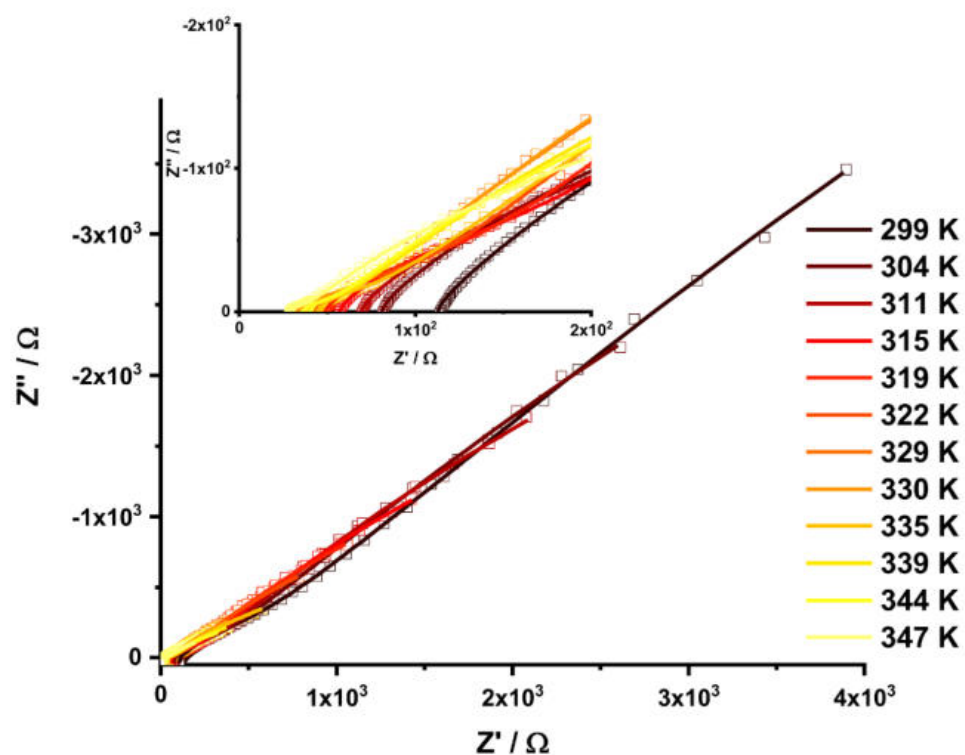


Figure S17. Nyquist plot of SPAF-2_{0.8}³³. The enlarged image section shows the bulk conductivity.

Table S18. Simulation parameters of the impedance measurements of SPAF-2_{0.8}³³. The equivalent circuit shown in Figure 2B was used and the sample thickness is 0.001 cm.

T / K	electrode			bulk/grain boundaries			electrode interface		
	R_{WL} / Ω	R_E / Ω	$L / 10^{-6} \text{ H}$	$R_{B/GB} / \Omega$	$CPE_{B/GB} / 10^{-5} \text{ S}$	$\alpha_{B/GB}$	$R_{EI} / k\Omega$	$CPE_{EI} / 10^{-4} \text{ S}$	α_{EI}
299	107(0)	--	1.36(2)	328(80)	3.13(33)	0.57(3)	47.3(42)	0.70(1)	0.55(1)
303	75.9(3)	--	1.58(1)	199(43)	4.12(43)	0.58(3)	27.8(28)	1.07(2)	0.54(1)
310	64.6(2)	--	1.65(1)	156(37)	4.90(37)	0.56(2)	16.1(8)	1.30(2)	0.54(0)
315	52.7(1)	--	1.70(1)	108(30)	6.53(50)	0.55(3)	11.5(4)	1.99(2)	0.53(0)
319	45.1(1)	--	1.74(0)	80.1(266)	8.21(76)	0.54(3)	6.31(21)	2.57(3)	0.55(0)
322	39.7(1)	--	1.75(0)	57.5(148)	9.95(97)	0.54(3)	4.43(13)	3.57(3)	0.54(0)
329	30.3(1)	--	1.78(0)	26.5(45)	19.9(22)	0.52(2)	1.95(7)	8.18(6)	0.53(0)
330	30.2(0)	--	1.78(0)	21.6(9)	16.6(13)	0.55(1)	1.97(6)	7.71(9)	0.52(0)
345	40.1(1)	--	1.74(0)	19.2(13)	9.22(12)	0.58(1)	2.43(8)	5.26(7)	0.49(0)
339	34.4(2)	--	1.76(0)	16.7(20)	26.5(37)	1.43(3)	1.43(3)	8.14(8)	0.49(0)
344	32.9(1)	--	1.76(0)	18.8(17)	35.4(40)	0.47(1)	1.19(2)	9.50(8)	0.48(0)
347	26.4(1)	--	1.78(0)	11.1(8)	58.1(89)	0.47(1)	0.74(1)	16.8(13)	0.48(0)

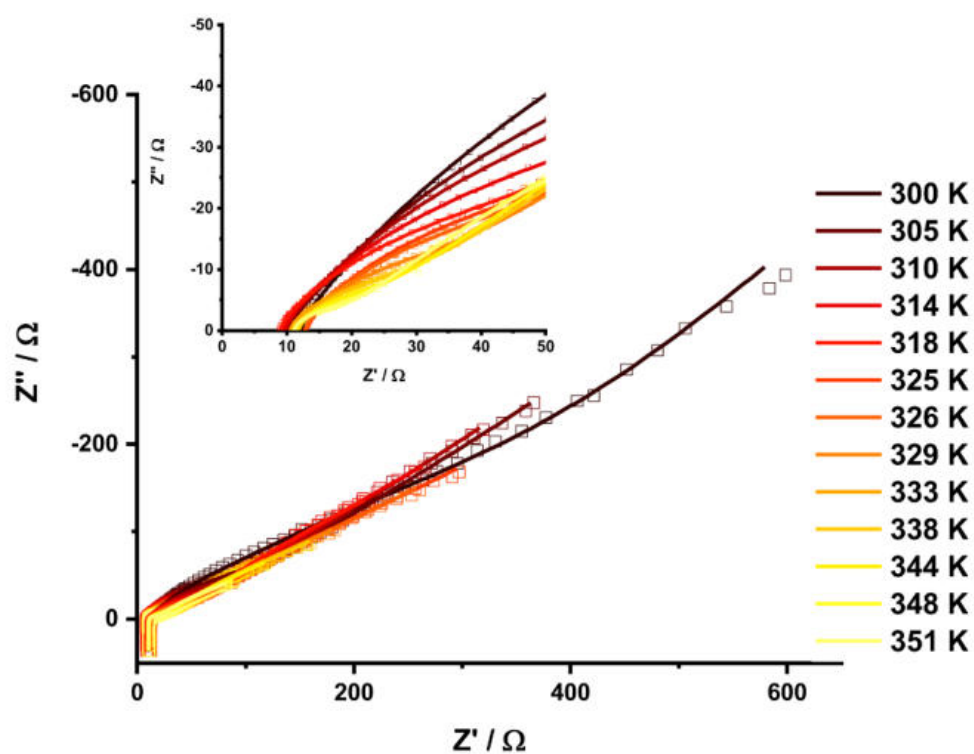


Figure S18. Nyquist plot of SPAF-2⁶⁷_{0.8}. The enlarged image section shows the bulk conductivity.

Table S19. Simulation parameters of the impedance measurements of SPAF-2_{0.8}⁶⁷. The equivalent circuit shown in Figure 2B was used and the sample thickness is 0.02 cm.

T / K	electrode			bulk/grain boundaries			electrode interface		
	R_{WL} / Ω	R_E / Ω	$L / 10^{-6} \text{ H}$	$R_{B/GB} / \Omega$	$CPE_{B/GB} / 10^{-4} \text{ S}$	$\alpha_{B/GB}$	$R_{EI} / k\Omega$	$CPE_{EI} / 10^{-3} \text{ S}$	α_{EI}
298	10.6 (0)	665 (86)	1.49 (0)	177(35)	1.60(5)	0.59(2)	2.58 (67)	0.516 (41)	0.57 (5)
306	9.16 (2)	746 (68)	1.49 (0)	102(10)	2.21(6)	0.59(1)	1.96 (36)	0.866 (43)	0.56 (3)
310	8.75 (2)	782 (68)	1.48 (0)	74.9 (60)	2.30(8)	0.60(1)	1.98 (33)	1.01 (4)	0.54 (2)
318	8.45 (2)	828 (70)	1.48 (0)	52.7 (34)	2.49(9)	0.60(1)	1.45 (17)	1.20 (4)	0.53 (1)
322	7.95 (2)	870 (72)	1.48 (0)	38.5 (21)	2.97(10)	0.59(1)	1.07 (10)	1.50 (4)	0.53 (1)
325	11.4 (0)	807 (88)	1.48 (0)	31.5 (26)	1.43(13)	0.63(1)	1.22 (10)	1.08 (3)	0.47 (1)
332	11.2 (0)	801 (83)	1.48 (0)	26.8 (24)	1.73(17)	0.62(2)	1.16 (10)	1.28 (4)	0.46 (1)
340	10.3 (0)	945 (85)	1.48 (0)	18.0 (12)	2.58(20)	0.61(1)	0.888 (70)	1.94 (5)	0.46 (1)
349	9.42 (2)	1081 (100)	1.48 (0)	13.3(7)	3.61(25)	0.59(1)	0.648 (46)	2.69 (6)	0.47 (1)
355	10.5 (0)	1197 (126)	1.47 (0)	12.4(7)	2.55(22)	0.61(1)	0.794 (51)	2.22 (4)	0.45 (1)

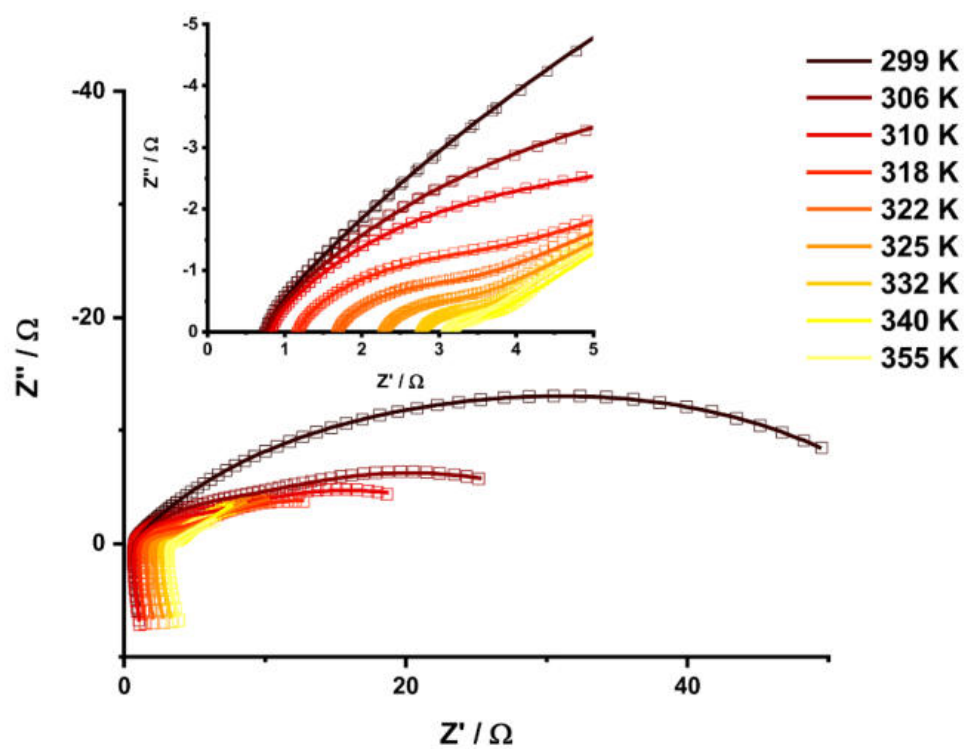


Figure S19. Nyquist plot of SPAF-2¹⁰⁰_{0.8}. The enlarged image section shows the bulk conductivity.

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Table S20. Simulation parameters of the impedance measurements of SPAF-2¹⁰⁰_{0.8}. The equivalent circuit shown in Figure 2B was used and the sample thickness is 0.10 cm.

T / K	electrode			bulk/grain boundaries			electrode interface		
	R_{WL} / Ω	R_E / Ω	$L / 10^{-7} H$	$R_{B/GB} / \Omega$	$CPE_{B/GB} / 10^{-4} S$	$\alpha_{B/GB}$	$R_{EI} / k\Omega$	$CPE_{EI} / 10^{-3} S$	α_{EI}
298	0.52(1)	71.1 (68)	6.67 (3)	22.9(9)	13.3(1)	0.60(0)	35.5(9)	3.49(11)	0.61(0)
306	0.41(3)	71.7 (135)	7.69 (9)	3.80(48)	8.45(136)	0.75(3)	33.3(8)	8.11(12)	0.45(1)
310	0.58(2)	105 (21)	8.10 (7)	3.16(25)	8.66(120)	0.72(2)	24.3(5)	11.6(1)	0.46(1)
318	0.99(2)	106 (19)	7.97 (6)	2.10(13)	13.5(2)	0.68(2)	19.4(4)	21.9(2)	0.47(1)
322	1.51(2)	93.0 (22)	7.89 (9)	1.17(13)	12.3(5)	0.71(5)	28.2(18)	40.1(11)	0.42(1)
325	2.13(3)	79.3 (26)	7.84 (12)	0.65(12)	8.30(698)	0.78(10)	71.0(243)	65.0(1)	0.39(2)
332	2.65(3)	67.9 (177)	7.79 (13)	0.39(6)	5.64(734)	0.84(14)	1E15	85.3(5)	0.39(0)
340	3.06(4)	60.5 (16)	7.69 (15)	0.26(6)	3.31(717)	0.89(22)	3.71E14	83.9(6)	0.42(0)
349	3.05(4)	56.0 (126)	7.70 (14)	0.14(6)	1.28(480)	1.00(37)	152	85.0(41)	0.44(1)
355	3.04(2)	54.6 (70)	7.70 (8)	0.18(4)	3.83(730)	0.89(19)	16.3(14)	88.9(30)	0.47(1)

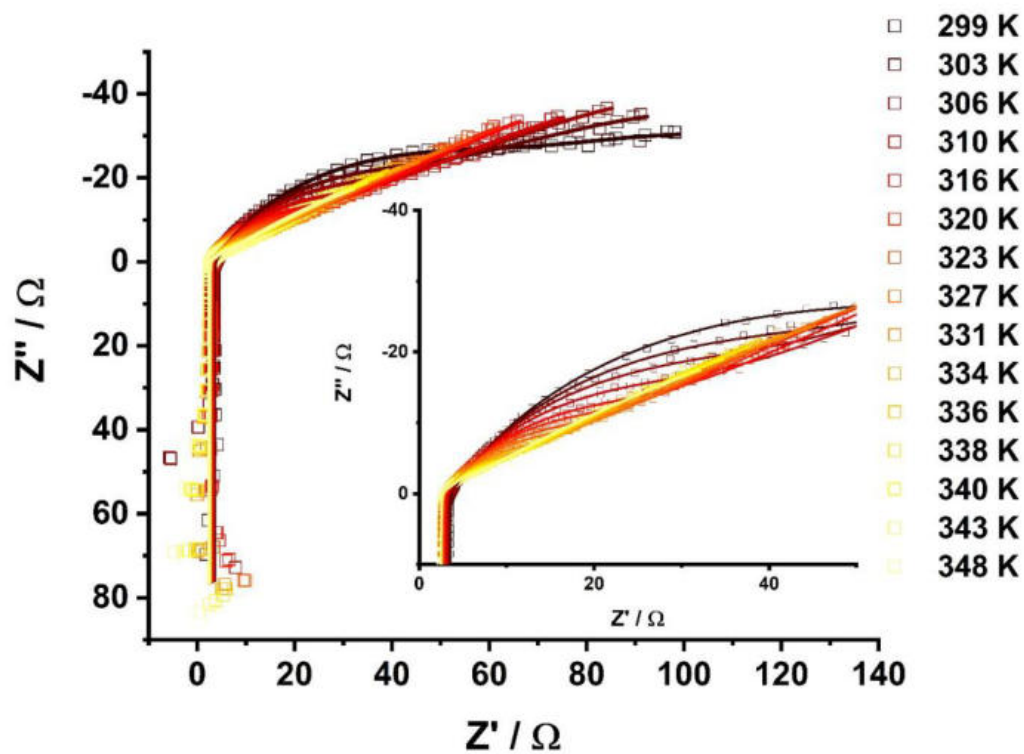


Figure S20. Nyquist plot of SPAF-2_{0.8} after water immersion. The enlarged image section shows the bulk conductivity and the results for simulations with the equivalent circuit shown in Figure 2B are given in Table S21.

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Table S21. Simulation parameters of the impedance measurements of SPAF-2_{0.8} after water immersion. The equivalent circuit shown in Figure 2B was used and the sample thickness is 0.35 cm.

T / K	electrode			bulk/grain boundaries			electrode interface		
	R_{WL} / Ω	R_E / Ω	$L / 10^{-7} \text{ H}$	$R_{B/GB} / \Omega$	$CPE_{B/GB} / 10^{-4} \text{ S}$	$\alpha_{B/GB}$	R_{EI} / Ω	$CPE_{EI} / 10^{-5} \text{ S}$	α_{EI}
299	3.50(1)	∞	1.21(1)	52.6(32)	4.53(14)	0.71(1)	117(6)	448(35)	0.56(1)
303	3.36(1)	∞	1.21(1)	35.5(18)	4.44(18)	0.75(1)	156(6)	397(18)	0.54(1)
306	3.20(1)	∞	1.21(1)	27.7(13)	4.54(21)	0.76(1)	192(9)	431(14)	0.52(1)
310	3.03(1)	∞	1.21(1)	21.1(9)	4.59(25)	0.78(1)	207(11)	498(15)	0.50(1)
316	2.83(1)	∞	1.21(1)	16.3(7)	5.05(32)	0.79(1)	248(17)	578(15)	0.49(1)
320	2.72(1)	∞	1.21(1)	12.6(6)	4.82(35)	0.81(1)	240(15)	597(14)	0.48(1)
323	2.62(1)	∞	1.21(1)	9.98(48)	5.10(43)	0.83(2)	222(14)	647(15)	0.48(1)
327	2.55(1)	∞	1.21(1)	8.15(41)	5.25(50)	0.84(2)	217(15)	718(16)	0.47(1)
331	2.46(1)	∞	1.22(1)	5.54(32)	5.32(64)	0.86(2)	189(12)	792(17)	0.46(1)
334	2.43(1)	∞	1.22(1)	4.17(27)	5.75(82)	0.88(2)	197(14)	877(18)	0.45(1)
336	2.44(1)	∞	1.21(1)	3.35(24)	6.60(111)	0.88(3)	213(17)	943(18)	0.44(1)
338	2.47(1)	∞	1.21(1)	2.63(20)	6.25(117)	0.90(3)	192(13)	955(17)	0.44(1)
340	2.43(1)	∞	1.21(1)	1.79(16)	6.75(162)	0.93(4)	179(12)	1046(18)	0.43(1)
343	2.40(1)	∞	1.21(1)	1.18(13)	7.15(228)	0.96(5)	167(11)	1137(19)	0.43(1)
348	2.38(1)	∞	1.21(1)	0.72(12)	10.3(49)	0.98(7)	171(12)	1245(20)	0.42(1)

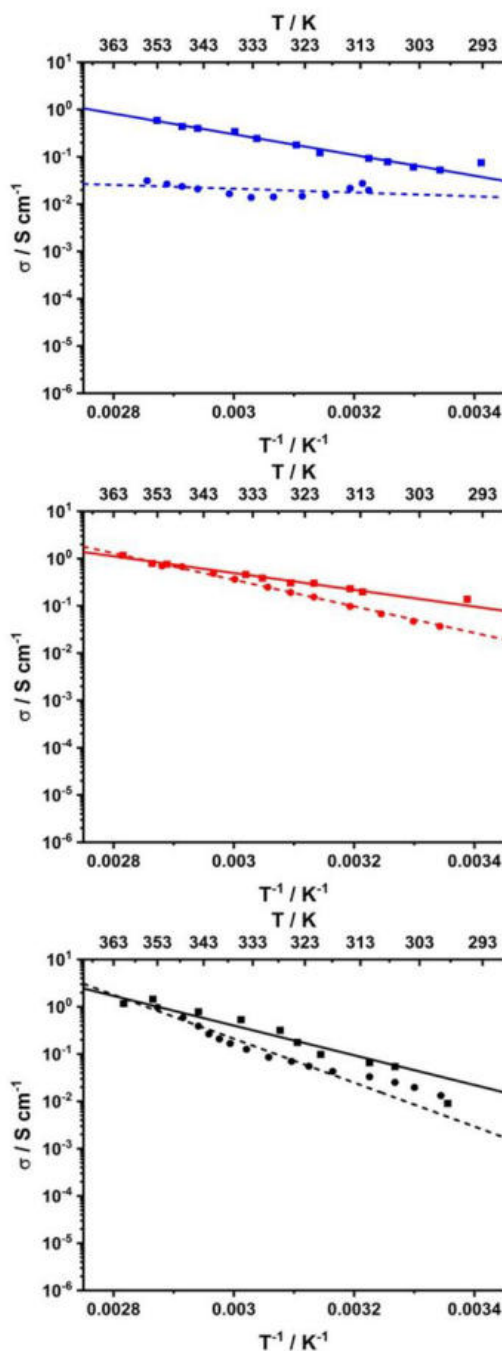


Figure S21. Arrhenius plots of the proton conductivities obtained after gas phase equilibration with 100 %RH (squares and solid lines) and water immersion (circles and dotted lines). SPAF-2_{0.3}, SPAF-2_{0.5}, and SPAF-2_{0.8} are given in blue, red, and green, respectively. The individual data are shown in Figures S12, S16, and S20 and Tables S13, S17, and S21.

S45

NMR measurements and characterization

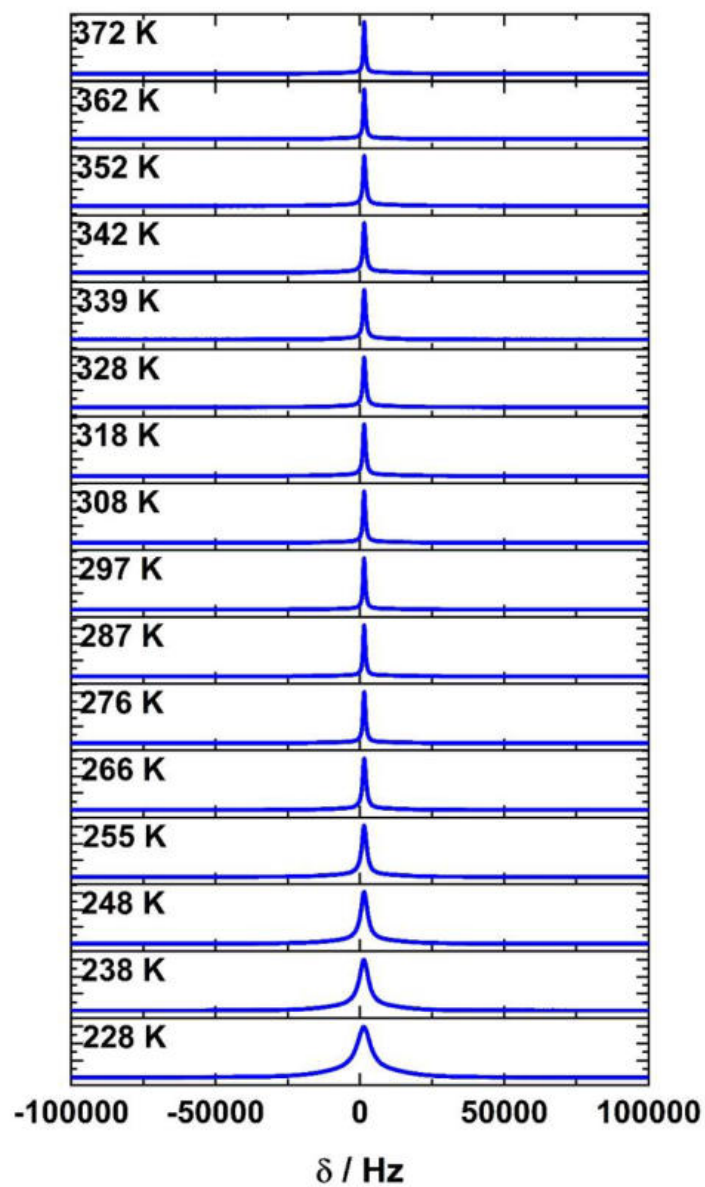


Figure S22. Wideline ^1H single-pulse NMR spectra of SPAF-2¹⁰⁰_{0.3}.

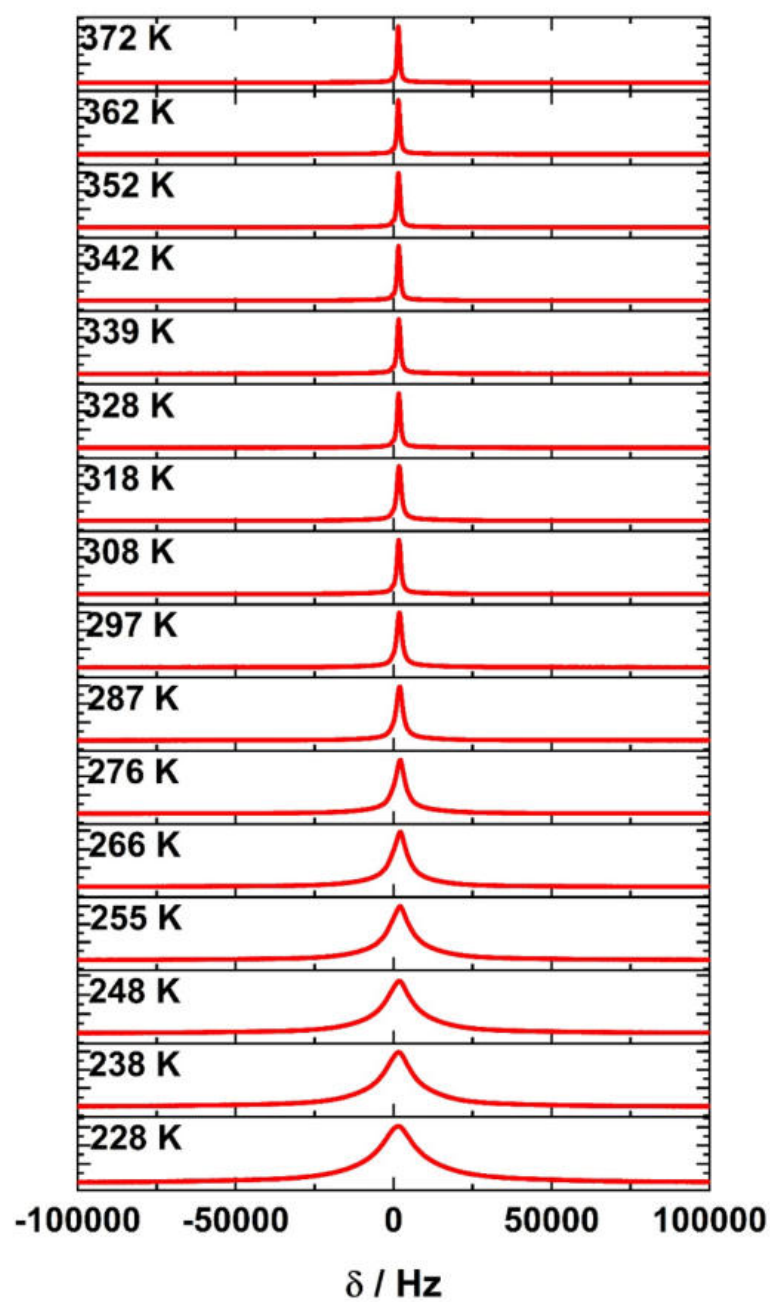


Figure S23. Wideline ^1H single-pulse NMR spectra of SPAF-2¹⁰⁰_{0.5}.

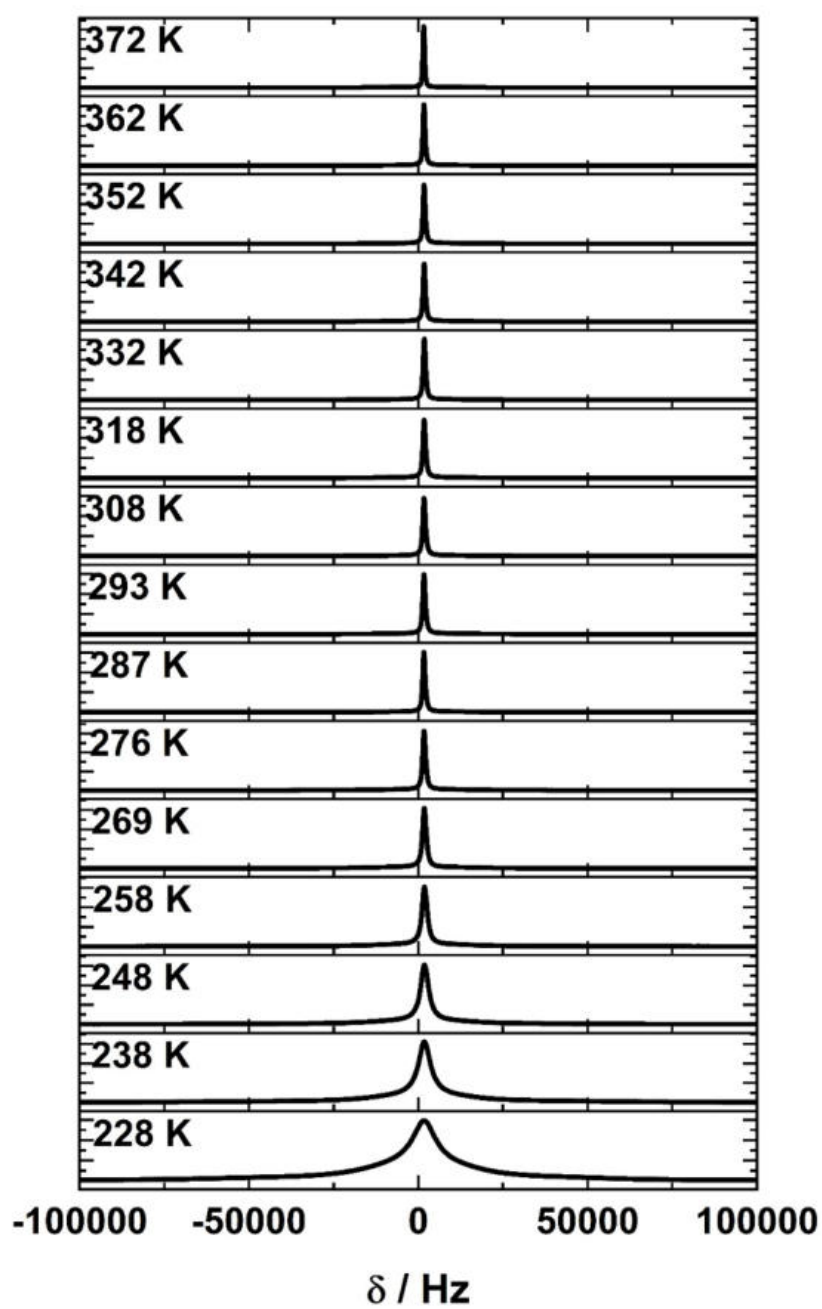


Figure S24. Wideline ^1H single-pulse NMR spectra of SPAF-2 $^{100}_{0.8}$.

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Table S22. Temperature-dependent trend of the Full width of half maximum (FWHM) of ^1H SP NMR spectra of SPAF-2 $^{100}_x$ (Figures S22-S24). The NMR spectra were deconvoluted with two Gaussian and one Lorentzian profile as described in the manuscript.

SPAF-2 $^{100}_{0.3}$				SPAF-2 $^{100}_{0.5}$				SPAF-2 $^{100}_{0.8}$			
T / K	FWH M_{mobile} / Hz	FWH M_{FW} / Hz	FWH M_{immobile} / Hz	T / K	FWH M_{mobile} / Hz	FWH M_{FW} / Hz	FWH M_{immobile} / Hz	T / K	FWH M_{mobile} / Hz	FWH M_{FW} / Hz	FWH M_{immobile} / Hz
228	5396	25855	66518	228	10941	27855	78408	228	7638	26614	82806
238	3862	26846	81747	238	8964	25598	85567	238	4314	26614	83226
248	2838	26401		248	8784	25914	85587	248	2853	26614	86424
255	2044	26135		255	7505	25786	78598	258	1821	26614	83731
266	1425	25955		266	5569	24386	7377	269	1304	26614	79891
276	1032	25486		276	4019	25116	74578	276	1039	26614	78652
287	889	24833		287	2530	23777	75097	287	862	25717	
297	920	24979		297	1988	25246		293	942	25571	
308	1000	24655		308	1640	30858		308	948	24702	
318	1078	23574		318	1309	25401		318	884	24364	
328	1166	23381		328	1170	24685		332	851	23948	
339	1164	23366		339	1062	25447		342	825	22718	
342	1100	22462		342	1036	23119		352	800	22524	
352	870	22297		352	952	23241		362	749	21748	
362	795	21639		362	871	23002		372	620	21209	
372	598	22115		372	744	24074					

Table S23. Relevant parameters for modeling the proton proportions of mobile ($p(\text{H}_2\text{O}_{\text{mo}})$) and immobile ($p(\text{H}_2\text{O}_{\text{im}})$) water molecules and framework protons ($p(\text{framework})$) as displayed in Figure 3B with eq (1).

x	$\Delta H^0 / \text{kJ mol}^{-1} \text{K}^{-1}$	$\Delta S^0 / \text{J mol}^{-1} \text{K}^{-1}$	p(framework)
0.3	17(1)	90	0.28
0.5	19(2)	85(10)	0.18
0.8	25(2)	107(10)	0.17

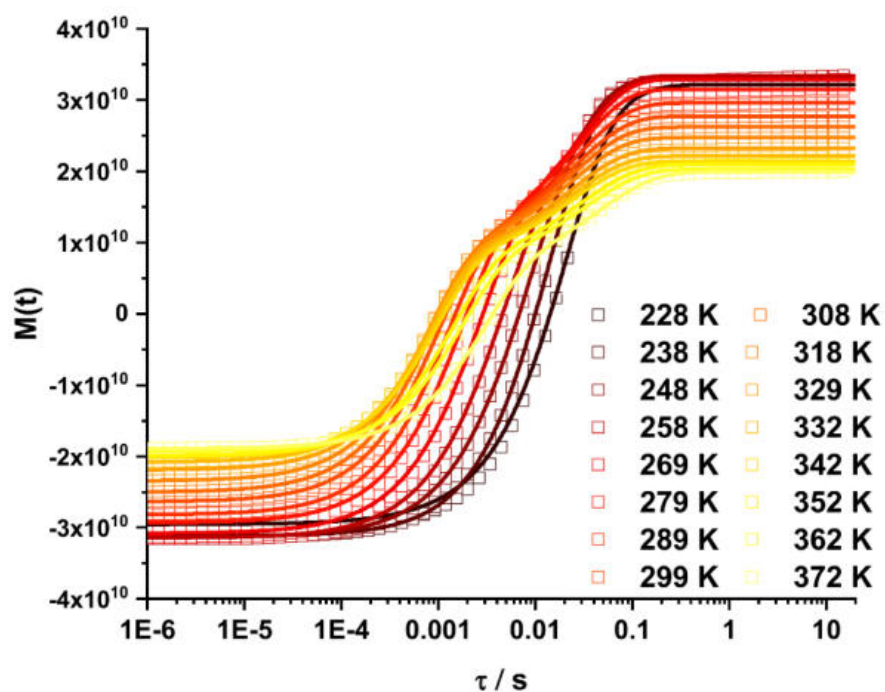


Figure 25. ^1H spin-lattice relaxation build-up curves of SPAF-2_{0.3}¹⁰⁰ acquired with an inversion sequence.

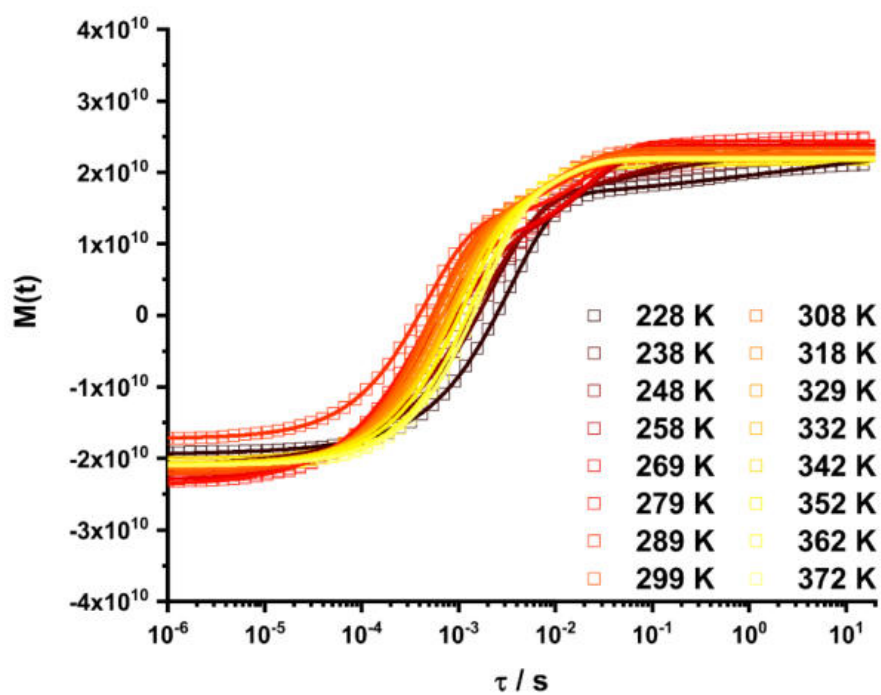


Figure S26. ^1H spin-lattice relaxation build-up curves of SPAF-2_{0.5}¹⁰⁰ acquired with an inversion sequence.

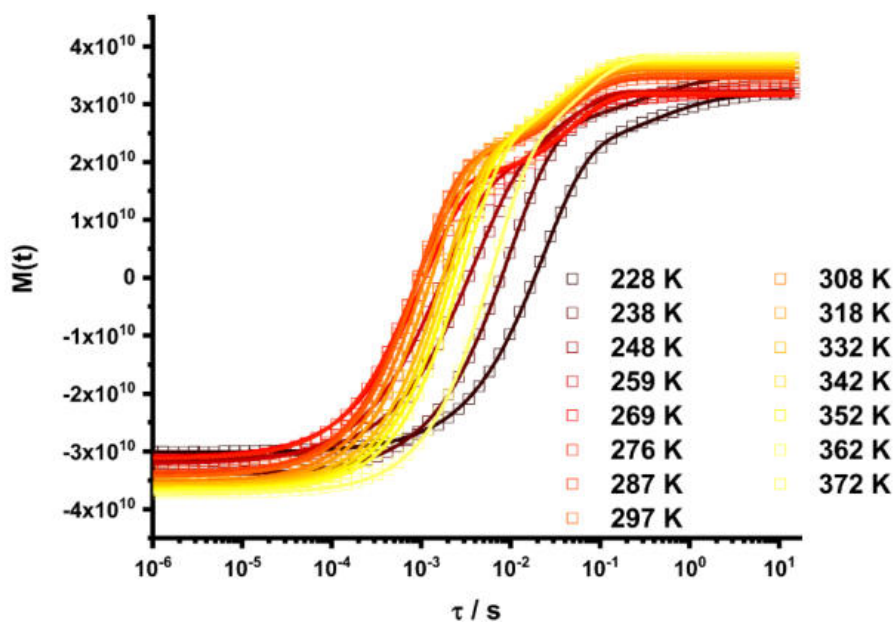


Figure S27. ^1H spin-lattice relaxation build-up curves of SPAF-2_{0.8}¹⁰⁰ acquired with an inversion sequence.

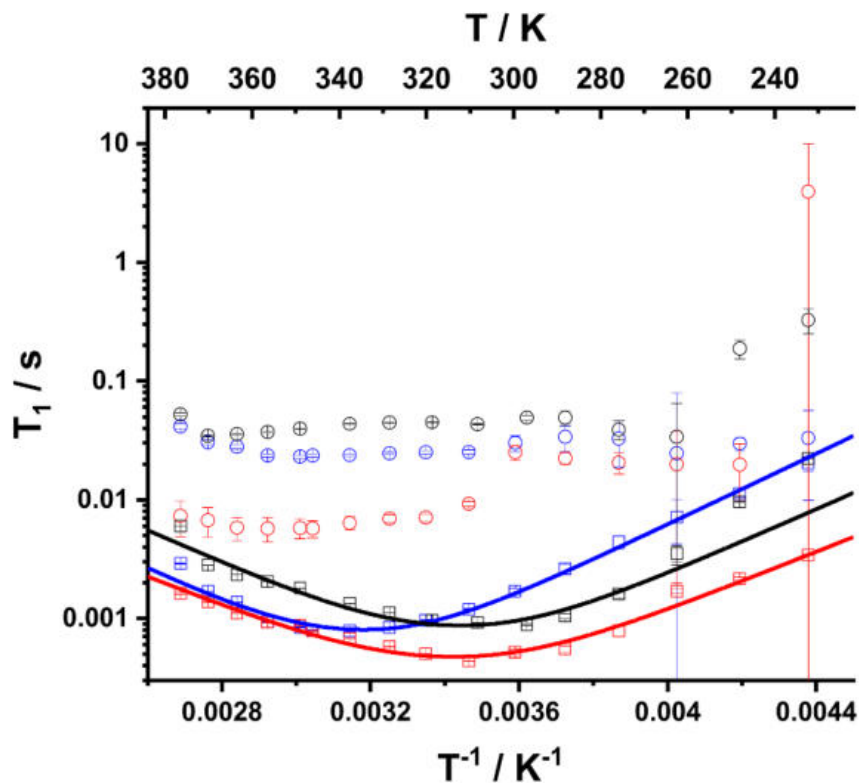


Figure S28. Arrhenius plot of T_1 times of SPAF-2_x¹⁰⁰ ($x = 0.3$ (blue), 0.5 (red), and 0.8 (black)) determined T_1 build-up curves (Figures S25-S27). Two T_1 times could be distinguished. Based on their relative proportions (Figure S29), the short component (squares) was assigned to the adsorbed water molecules. The longer T_1 describes the relaxation of the framework protons (circles). The BPP-type trend curves for the shorter T_1 component are intended as guide for the eye.

Table S24. Analysis of the temperature-dependent T_1 data for SPAF-2_x ($x = 0.3, 0.5, 0.8$) all equilibrated at 100% RH. Prefactors C were derived from analyzing the short component of the spin-lattice relaxation data (Figure S28) with eq(2). $J_{\text{trans}}(\omega_1, \tau_{\text{trans}})$ was numerically solved for series of τ_{trans} to match the observed T_1 data. The determined τ_{trans} are given in Figure 3D.

x	C
0.3	8.58×10^{12}
0.5	1.53×10^{13}
0.8	7.56×10^{12}

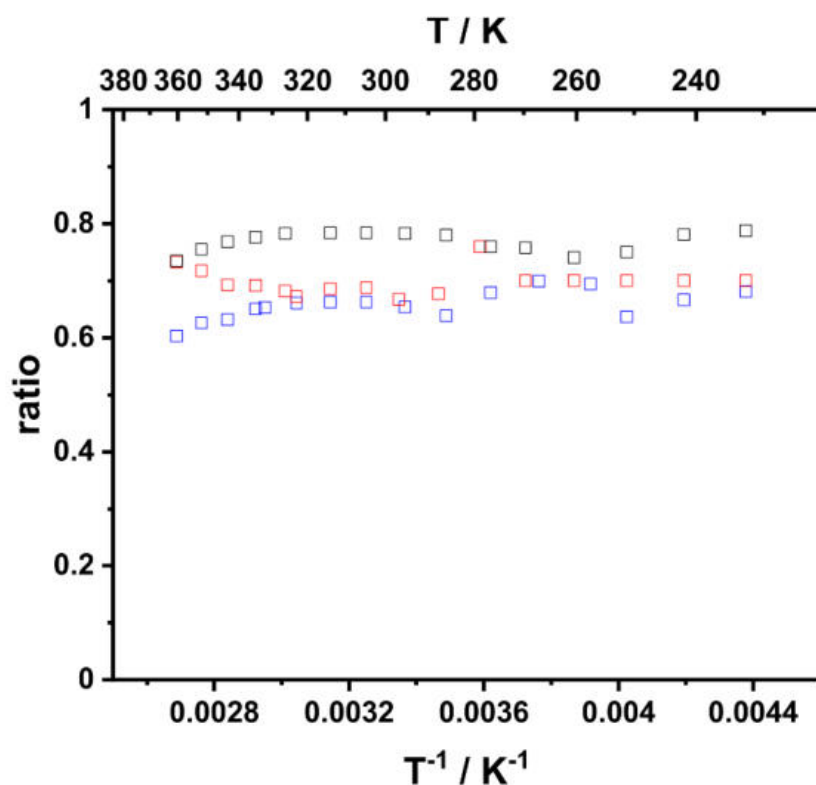


Figure S29. Ratio of the intensities of the water to network protons of SPAF-2_x¹⁰⁰ ($x = 0.3$ (blue), 0.5 (red), and 0.8 (black)). The ratio was determined by refining the T_1 build-up curves shown in Figures S25-S27 with two exponential relaxation functions.

¹H NMR spin-lattice relaxation rates under the influence of paramagnetic centers

The ¹H NMR spin-lattice relaxation rates of a mobile species, in our case water molecules and oxonium ions moving fast along immobilized paramagnetic centers is mainly driven by the heteronuclear dipole interaction between the magnetic moments of ¹H nuclei on the water molecules and the ones representing the paramagnetic centers.^{14,15} For the present work, the latter consist most likely of residual Fe³⁺ ions, trapped in the framework during synthesis. The rates follow eq S1

$$\frac{1}{T_1} = \frac{2}{15\pi} S(S+1) \left(\frac{\mu_0 \hbar}{4\pi} \right)^2 \gamma_I^2 \gamma_S^2 (J(\omega_I - \omega_S) + 3J(\omega_I) + 6J(\omega_I + \omega_S)). \quad (S1)$$

γ_I and γ_S are the gyromagnetic ratios of protons (I) and the paramagnetic iron centers (S). ω_I and ω_S denote the Larmor frequencies of protons and the unpaired electrons of the iron ions and $J(\omega)$ describes the spectral density of the water motion which contains both translational and rotational contributions. For the aqueous environment of SPAF-2_x at 100 % RH, Fe³⁺ ions will exhibit a high-spin state. Thus, S equals 5/2 and, in the spin-only approximation, the gyromagnetic ratio of the iron ions is given by $\gamma_S = \sqrt{S(S+1)}\gamma_e$ with γ_e being the gyromagnetic ratio of free electrons. Considering further that $\omega_I \ll \omega_S$, the following relation holds $J(\omega_I - \omega_S) \approx J(\omega_I + \omega_S) \approx J(\omega_S)$. Eq S1, thus, simplifies to

$$\frac{1}{T_1} = \frac{2}{15\pi} (S(S+1))^2 \left(\frac{\mu_0 \hbar}{4\pi} \right)^2 \gamma_I^2 \gamma_e^2 (3J(\omega_I) + 7J(\omega_S)) \quad (S2)$$

With respect to the paramagnetic centers rotational motion of the water molecules and oxonium ions are usually ineffective^{15,16} and translations on the order of a few nanometers are required to reach an efficient correlation loss. Thus we model $J(\omega)$ by a purely translational spectral density. For simplicity, we use the hydrodynamic FFHS model. Here the protons of the water molecules are located in the center of a hard sphere. Its diameter d represents the distance of the closest possible approach to the Fe³⁺ ions and the water molecules show a force-free diffusion.¹⁶ The fluctuating distance contributions merely modulate the spectral density and $J(\omega)$ merges into

$$J(\omega) = \frac{16\pi}{9} \cdot \frac{N_S}{d^3} J_{trans}(\omega) \quad (S3)$$

$$\text{with } J_{trans}(\omega, \tau_{trans}) = \frac{54}{\pi} \int_0^\infty \frac{u^2}{81+9u^2+2u^4+u^6} \frac{u^2 \tau_{trans}}{u^4+(\omega \tau_{trans})^2} du \quad (S4)$$

and N_S being the Fe³⁺ ion density. For systems like water and within the accessed temperature range for this work, $J_{trans}(\omega_I) \gg J_{trans}(\omega_S)$ holds as most fluctuations are limited to the nanosecond time scale (e.g. at the temperature of the T_1 minimum $J_{trans}(\omega_I)$ is more than five orders larger than $J_{trans}(\omega_S)$). The spin-lattice relaxation rate is then given by

$$\frac{1}{T_1} = \frac{32\pi}{45} (S(S+1))^2 \left(\frac{\mu_0 \hbar}{4\pi} \right)^2 \gamma_I^2 \gamma_e^2 \frac{N_S}{d^3} (J_{trans}(\omega_I, \tau_{trans})) \quad (S5)$$

Proton number densities

The number density of the protons n_x in SPAF-2_x is given by

$$n_x = \frac{IEC \cdot N_A}{V_P} \quad (S6)$$

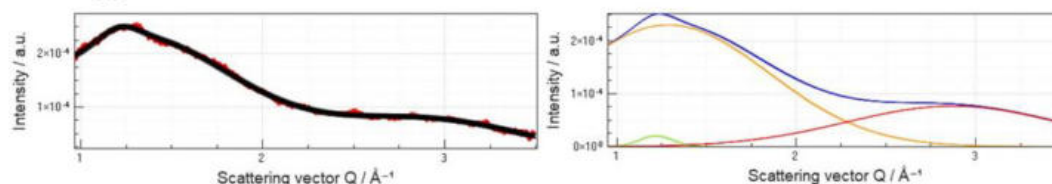
The equation contains the ion exchange capacity (IEC), Avogadro constant N_A and the specific active pore volume V_P , calculated from physisorption measurements of PAF-2 with the assumption that the pore volume of hydrated SPAF-2_x is similar to that of PAF-2 (Figure 1B) and $1 \text{ cm}^3 \text{ g}^{-1}$ for the density of the adsorbed water.

Table S25. Number densities n_x for SPAF-2_{0.3}¹⁰⁰, SPAF-2_{0.5}¹⁰⁰, and SPAF-2_{0.8}¹⁰⁰.

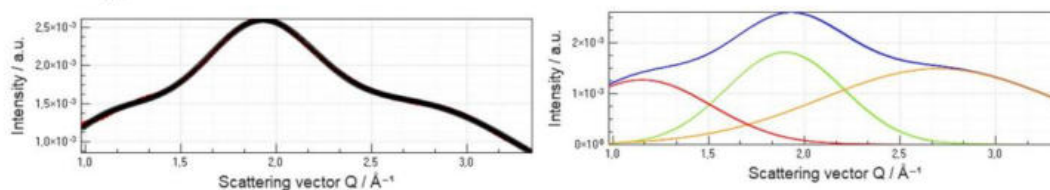
x	n_x / m^{-3}
0.3	8.58×10^{12}
0.5	1.53×10^{13}
0.8	7.56×10^{12}

WAXS measurements

SPAF-2_{0.3}



SPAF-2_{0.5}



SPAF-2_{0.8}

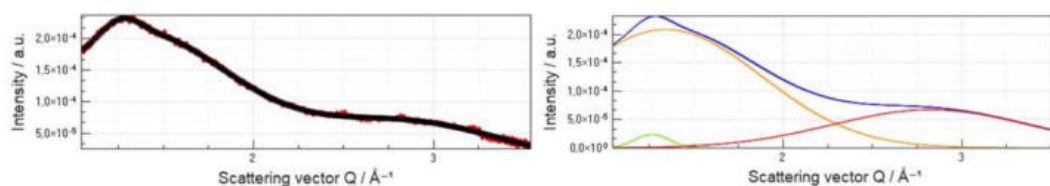


Figure S30. WAXS measurements of SPAF-2_x (left) and the fitted Gaussian functions (right). The peak maxima are summarized in Table S26.

Table S26. Scattering vector and calculated distances from WAXS measurements (Figure S30) of SPAF-2_x.

framework	Scattering vector Q / Å ⁻¹	Distance / Å
SPAF-2 _{0.3}	1.27	4.95
	1.34	4.69
	2.82	2.22
SPAF-2 _{0.3}	1.15	5.46
	1.90	3.30
	2.70	2.33
SPAF-2 _{0.3}	1.22	5.46
	1.29	4.87
	2.87	2.19

Synthesis and characterization of educts

Tetraphenylmethane

A suspension of 9.16 g (98.4 mmol, 2.7 eq.) aniline and 10 g (35.9 mmol, 1 eq. chlorotriphenylmethane is heated to 180 °C for 30 min. After crushing the formed violet solid it is dissolved in a mixture of 60 ml methanol and 40 ml 2 M hydrochloric acid. The solution is heated up for 30 min to reflux and filter. The dried solid is dissolved in dimethylformamide and at -15 °C 8.2 ml (61.0 mmol, 1.7 eq.) isoamyl nitrite, 10.8 ml sulfonic acid, and 18 ml (0.4 mmol, 11 eq.) phosphinic acid is given to it. Under gas evolution, the solution is heated up to 50 °C for 16 h and filtered. The corresponding solid is washed twice with dimethylformamide, water, and ethanol, and dried under reduced pressure. The yield was 10.5 g corresponding to 32.7 mmol (91 %). The purity was verified by EA, IR, and liquid-state NMR spectroscopy (Figures S31-S33).

CHNS [wt.-%]: C [92.21], H [6.40], N [0.11], S [0.17]; Calc. C [93.71], H [6.29], N [0.00], S [0.00]

FT-IR (ATR): ν [cm⁻¹] = 3080, 3059, 3030, 1591, 1491, 1440, 1396, 1323, 1226, 1182, 1155, 1128, 1080, 1036, 1002, 987, 939, 844, 765, 750, 700, 634, 619, 581, 525, 491

¹H-NMR (500 MHz; DMSO-d₆): δ [ppm] = 7,3 (t, 1H, H-4), 7,2 (t, 1H, H-5), 7,1 (t, 1H, H-3)

¹³C NMR (500 MHz, DMSO-d₆): δ [ppm] = 146,8 (C-2), 131,0 (C-3), 128,2 (C-4), 126,5 (C-5), 34,8 (C-1)

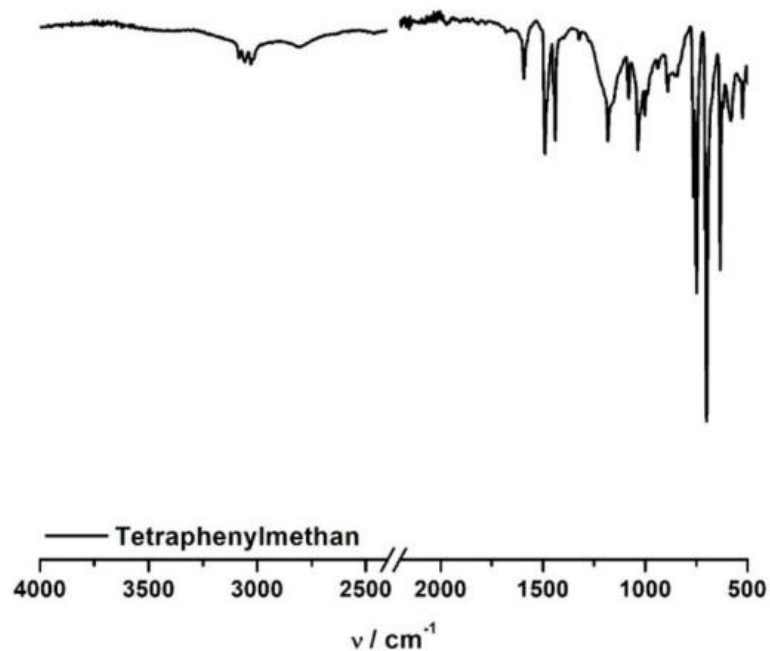


Figure S31. IR spectrum of tetraphenylmethane.

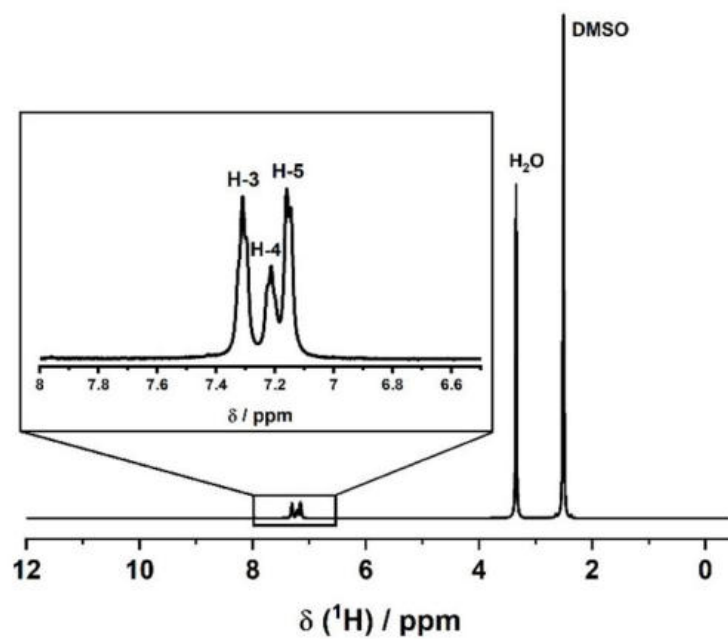


Figure S32. Liquid-state ^1H NMR spectrum of tetraphenylmethane.

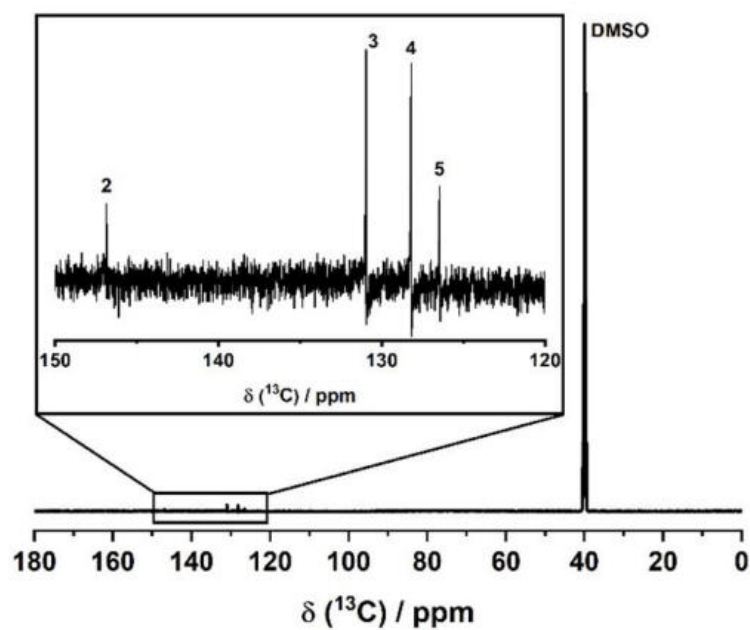


Figure S33. Liquid-state ^{13}C NMR spectrum of tetraphenylmethane.

Tetrakis(4-bromophenyl)methane

After drying 9 g (28.1 mmol, 1 eq.) tetraphenylmethane at 125 °C for 16 h and separation under argon atmosphere, 28.77 g (561.8 mmol, 20 eq.) Br₂ was added to the solid at 0 °C. The reaction was stirred for 1.5 h at this temperature and afterward, it was cooled to -70 °C. At 70 °C 125 ml ethanol was dropped to the reaction and it was allowed to reach room temperature overnight. To neutralize the excess of bromine an aqueous sodium bisulfite solution was given to the solution. The solid was filtered, washed with water, dried, and recrystallized in chloroform/ethanol mixture (1:1) to get a beige-colored solid. The yield was 17.3 g corresponding to 27.4 mmol (98 %). The purity was verified by EA, IR, and liquid-state NMR spectroscopy (Figures S34-S36).

CHNS [wt.-%]: C [45.73], H [2.45], N [0.13], S [0.17]; Calc. C [47.21], H [2.54], N [0.00], S [0.00]

FT-IR (ATR): ν [cm⁻¹] = 3083, 3060, 3024, 1908, 1580, 1455, 1396, 1371, 1185, 1113, 1074, 1007, 876, 809, 748, 691, 678, 632, 533, 500

¹H-NMR (500 MHz, DMSO-D₆): δ [ppm] = 7.54 (d, 1H, H-3), 7.06 (t, 1H, H-4)

¹³C-NMR (500 MHz, DMSO-D₆): δ [ppm] = 145.00 (C-2), 132.85 (C-4), 131.62 (C-3), 120.46 (C-5), 63.76 (C-1)

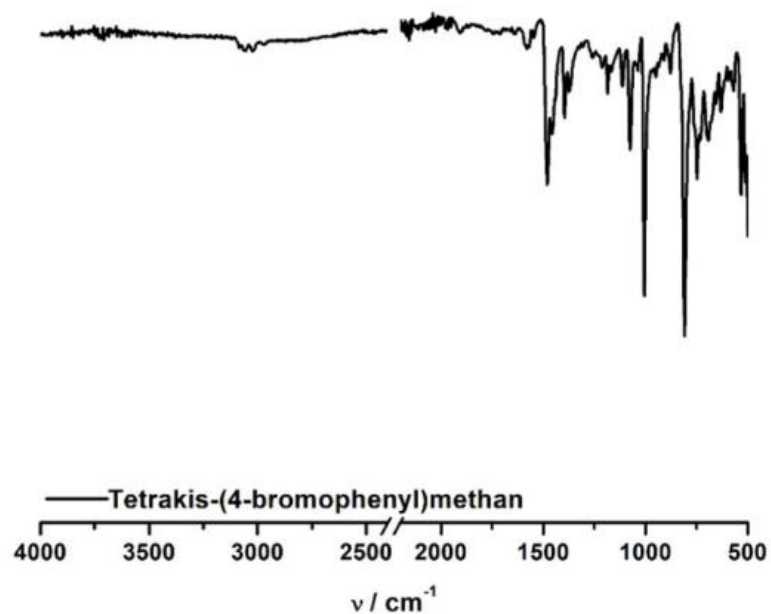


Figure S34. IR spectrum of tetrakis(4-bromophenyl)methane.

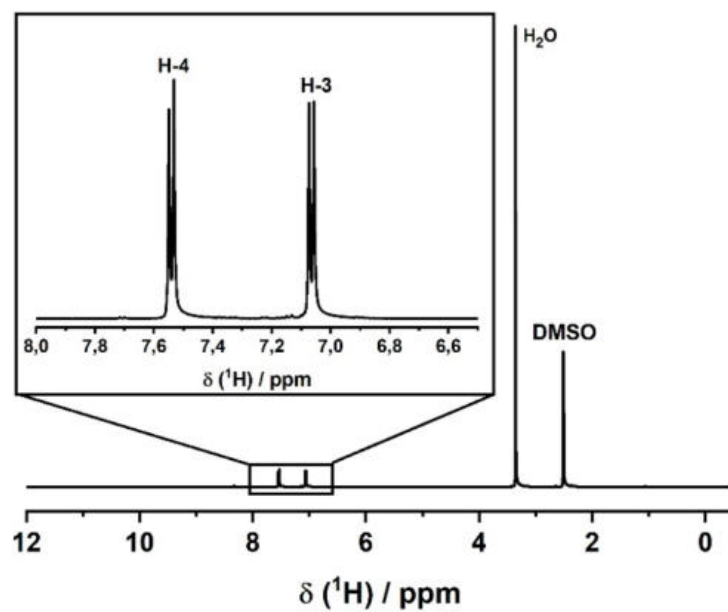


Figure S35. Liquid-state ^1H NMR spectrum of tetrakis(4-bromophenyl)methane.

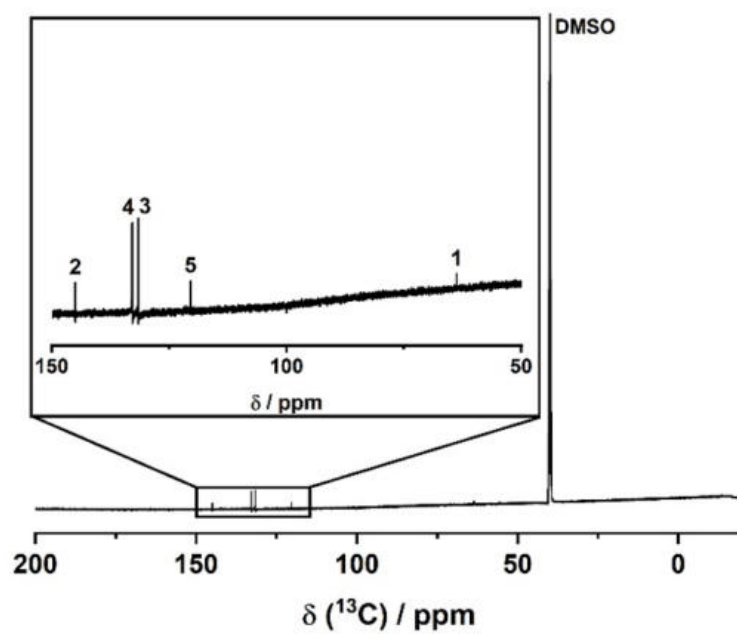


Figure S36. Liquid-state ^{13}C NMR spectrum of tetrakis(4-bromophenyl)methane.

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Ultrafast Proton Conduction in an Aqueous Electrolyte Confined in Adamantane-like
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4.2. Understanding of Proton Conduction in Confinement of SPAF-303

Understanding of Proton Conduction in Strong Confinement

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Keywords: covalent organic framework; porous aromatic framework, method, Charge Transport, Nuclear Magnetic Resonance Spectroscopy, impedance spectroscopy, paramagnetic>

Abstract

Proton conduction in microporous frameworks is an essential component of membrane materials such as used in fuel cells. In this study, we take a closer look at the new method of combining NMR spectroscopy and impedance spectroscopy to clarify the mechanism for proton conduction in confinement. For this analysis the sulfonated porous aromatic framework (SPAF-303_x) with a sulfonation degree *x* of 30 %, 50 %, and 100 % at relative humidity (RH) conditions of 33 % and 67 % is used. ¹H nuclear magnetic relaxation (NMR) spectroscopy gives insights in the water subensembles inside the pores and spin-lattice relaxation measurement enabled to calculate the correlation times and diffusion coefficients for the microscopic scale. By Nernst-Einstein equation it is transferred to the conductivity which is compared with the macroscopic measured by impedance spectroscopy (EIS). This comparison gives the limitation of diffusion through the framework by bottlenecks between the pores. The NMR spectroscopy investigations underling the high microscopic conductivity of the confinement in H₂O@SPAF-303_x which is about 10⁻⁹ m² s⁻¹. Moreover, the presence of two water regimes inside the pores clarified that the exchange between a mobile regime and an immobile regime, which is strongly bound to the sulfonic acid groups of the framework, is, besides the bottlenecks, the determining influence for the proton conduction at 33 % RH and 67 % RH. The application of these combined investigation methods demonstrates the possibility of how new materials can be further developed and engineered in the future.

Introduction

Proton conduction is a fundamental process with significant implications in various scientific and technological domains, including energy conversion, fuel cells, and biochemical systems.^[1] Understanding the mechanisms behind proton transport is essential for the development of advanced materials that can efficiently facilitate this process. Proton conduction typically occurs in bulk and liquids via two mechanisms. The vehicle mechanism, where protons are carried by water or other molecules, and the Grotthuss mechanism, where protons hop between hydrogen-bonded networks of water molecules.^[1–3] The latter mechanism, which involves the relay of protons through a hydrogen-bonded network. These mechanisms often exhibit high degrees of structural symmetry, long-range order, and isotropic diffusion pathways, enabling the formulation of well-defined transport models and relaxation dynamics.^[2–6] These insights have inspired the design of synthetic materials for proton transport^[7–10] with several classes of materials like polymers^[11], ceramics^[12], silica materials^[13], covalent organic frameworks^[14], and hybrid materials^[15] were developed and have been studied for their proton conduction properties.

For instance, Nafion, a perfluorosulfonic acid polymer, has been extensively researched for its high proton conductivity and stability in fuel cells and is the material that has been used commercially to date.^[16,17] The high proton conductivity and mechanical properties of Nafion depend strongly on the hydration level of the membrane. Because of this fact, complex water management is necessary.^[18,19] That requires an external humidification and a special air flow of the reactant gases so that the hydration level λ of the membrane is higher than two.^[19] At these hydration levels the adsorbed water is stored in a moderate confinement. This confinement leads to a heterogeneous dynamic for the water molecules such as anisotropic diffusion like strongly bounded water interacting with the sulfonic acid groups and bulk-like water which is in the channel core.^[1,20] This observation is also found by multiple dynamical regimes for the bulk-like water and the slower components associated with interfacial water.^[21] The aforementioned classes of materials attempt to solve the problem of water management and the associated limitation of the working temperature up to 353 K.^[6,16,22,23]

To establish a new proton-conducting material for a fuel cell, it is not only necessary to determine the maximum proton conductivity, but also the exact mechanism of conductivity. The group of Senker focuses their research on the material group of PAF, especially PAF-1 and PAF-303 with a high hydration level of about 100 % RH that leads to a fully loaded pore

volume.^[24–27] The sulfonation of PAF-303 via gas phase sulfonation with oleum leads to different sulfonation degrees, whereas the arrangement of the sulfonic acid groups occurs independently due to steric and charge effects into the pore. This results in self-organization of sulfonic acid groups. The proton conduction of SPAF-303 goes up to 1 S cm^{-1} at 353 K and 100 % RH.^[26] The underlying transport mechanism is based on a vehicle mechanism with a high self-diffusion coefficient of about $10^{-9} \text{ m}^2 \text{ s}^{-1}$ for water. The water is stored in nanometer-sized pores in the SPAF-303. In the connected pore system are two regions of water regimes. One is strongly bound to the SO_3^- groups and the other one is a highly mobile phase inside the pore. The two regimes are in thermal equilibrium that water and oxonium molecules can exchange between these. With increasing temperature, the mobile phase rises. Moreover, the research suggests that a homogenous distribution of sulfonic acid groups for a sulfonation degree of 50 % for SPAF-303_{0.5} leads to a minimized energy level for charge and mass transport through the confinement. This reduced energy is caused by the nanostructure of the framework. The pore walls are structured by alternating hydrophilic and hydrophobic groups at a sulfonation degree of 50 %.

In this study, the paramagnetic frameworks SPAF-303 are examined more closely regarding their proton conductivity mechanism. For this purpose, the frameworks with sulfonation degrees of 30 %, 50 % and 80 %, with their diamond-like lattice, are measured at a relative humidity of 33 and 67% RH using NMR spectroscopy. The measured NMR-spectra are analyzed for their line shape to ascertain the water regimes in the pores and the relaxation times are determined to calculate the conductivity using the method published by Winterstein et al.^[26] The calculated conductivity is compared with the conductivity from impedance measurement, to clarify the resulting conduction mechanism.

Experimental section

The chemicals and solvents which are used in this study were commercially available and were of reagent grade without further purification. All samples are synthesized and characterized to the protocol of Winterstein et al.^[26] and added to the Supporting Information.

Water physisorption measurements were done at 293 K on an AsiQ-MP-MP-AG setup (Anton Paar QuantaTec, BoyntonBeach, USA). The samples were degassed at 393 K for 12 h. The software package ASIQ ver. 3.0 was used for data export. The saturated samples at 33, 67 and 100 % RH for 24 h were measured with a TA Instrument Discovery DSC 2500 to receive a thermogram. Under nitrogen atmosphere the temperature range was set to 193 to 353 K with a

heating and cooling rate of 5 K min⁻¹ with three cycles. The third cycle was used for the evaluation. The sulfonation degree was determined by titration with an aqueous 10 mM NaOH solution and a Mettler Toledo seven2go pH meter.

The samples were dried under reduced pressure and heated to 393 K for 24 h. The dried samples were placed in the NMR tube and stored under controlled humidity. The relative humidity was set by a saturated salt solution. An activation of the samples was not necessary. The NMR tubes were sealed with a glass spacer and UV glue.

All solid-state NMR spectra were performed on a Bruker Avance III HD spectrometer with a B₀ field of 7.0 T ($\gamma(^1\text{H}) = 300$ MHz). All ¹H spectra were referenced to residual proton signal in D₂O. The Single pulse experiments were performed with a 90° pulse with 1.7 to 1.8 μ s pulse length and a power level of 400 W. The recycle delay was set to 5 s. The spin-spin relaxation measurements were done with inversion recovery sequence. The pulse length of the 180° pulse was 3.6 μ s at a power level of 400 W.

Characterization

The three microporous frameworks (see for further information the Supporting Information) with a sulfonation degree of 30 % (SPAF-303_{0.3}), 50 % (SPAF-303_{0.5}), and 80 % (SPAF-303_{0.8}) were equilibrated at 33 % RH and 67 % RH. The λ values for 33 % RH are 1.6 (x = 0.3), 2.5 (x = 0.5), and 1.7 (x = 0.8) (Figures S1, S2). At 67 % RH the λ values rise to 6.2 (x = 0.3), 4.4 (x = 0.5), and 3.1 (x = 0.8) (Figures S1, S2). Equal to the publication of Winterstein et al.^[26] the water content is rising from 30 % sulfonation degree to 80 %. ¹H NMR spectra of the three different frameworks at 33 % RH are shown in Figure 1 A-F. The low-temperature measurements at about 220 K contain three overlapping resonances, with two of the three resonances being broad. The refined deconvolution of the two components was done with a Gaussian profile and the third one with a Lorentzian profile. The Gaussian indicates for these two components an anisotropic orientation due to the magnetic field, whereas the Lorentzian-

type is caused by an isotropic and fast reorientation of the water molecules.

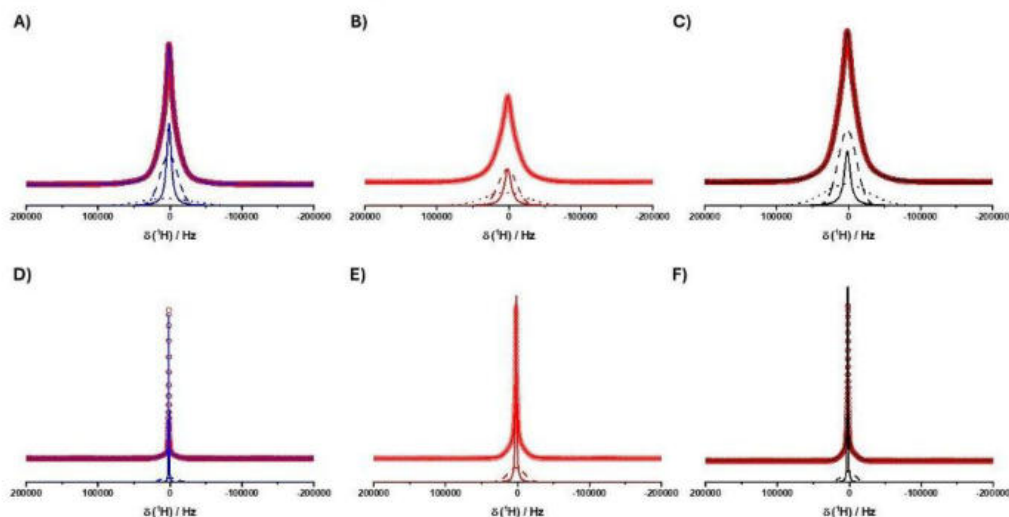


Figure 1: ^1H single pulse NMR spectrum of SPAF-303_x ($x = 0.3$ (blue), 0.5 (red), and 0.8 (black)) at 33 % RH. The spectra were fitted (red circles) with three superimposing signals. The solid line shows the mobile phase (fwhm < 10 kHz), the dashed line represents the framework (fwhm $\approx$ 25 kHz), and the dotted lines give the bound water (fwhm $\approx$ 80 kHz). Figures A-C are measured at the lowest temperature ($T \approx 220$ K) and D-F at the highest temperature ($T \approx 370$ K).

The full widths at half-maximum (fwhm) are for the broad resonances of about 25 kHz and 80 kHz and the narrow is <10 kHz. The observed resonances can be assigned analogously to the resonances of the spectra at 100% RH of SPAF-303_x.^[26] The framework is represented by the 25 kHz broad component, which is temperature-independent, and the water is given by the two other resonances. The broad Gaussian-type resonance of water (fwhm $\approx$ 80 kHz) keeps with increasing temperature its fwhm whereas the sharper resonance decreases its fwhm. At higher temperatures, shown in Figure 1 D-F, the spectra contain only two components (Table S1). The broader component of water with about 80 kHz decreases in intensity until it no longer exists, the smaller component <10 kHz rises and is getting a smaller fwhm (Table S1). The narrow line shape indicates a faster reorientation of the water molecules in the pores.

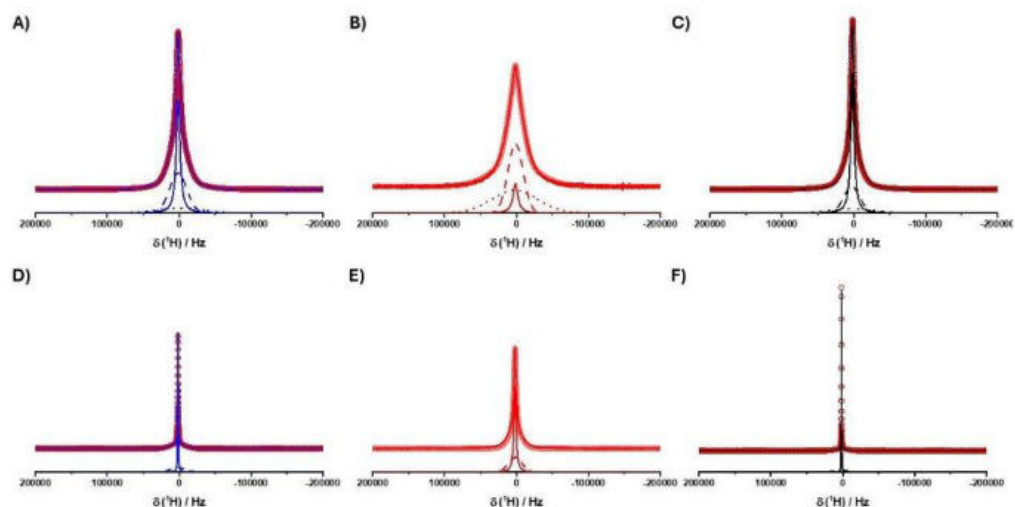


Figure 2: ^1H single pulse NMR spectrum of SPAF-303 $_x$ ($x = 0.3$ (blue), 0.5 (red), and 0.8 (black)) at 67 % RH. The spectra were fitted (red circles) with three superimposing signals. The solid lined showing the mobile phase (fwhm < 10 kHz), the dashed line represents the framework (fwhm ≈ 25 kHz), and the pointed lines giving the bound water (fwhm ≈ 80 kHz). The figures A-C are measured at the lowest temperature ($T \approx 220$ K) and D-F the highest temperature ($T \approx 370$ K).

The frameworks SPAF-303 $_x$ equilibrated at 67 % RH (Figure 2, Table S3) showing the same results and behavior as the frameworks as already mentioned in Figure 1. At both relative humidities, the determined ratio of protons of the adsorbed water to protons of frameworks fits very well with the calculated ratio from the water physisorption measurement (Table S3). For both relative humidities the broader component decreases much faster for sulfonation degrees of 0.3 and 0.8 with increasing temperature than for 0.5 (Figure 3). For 33 % RH the sharp water component reaches its maximum at about 280 K and for 67 % RH at about 260 K. The sulfonation degree of 0.5 gives the whole temperature range at 33 % RH a broad component. This component was only fittable to about 265 K. At higher temperatures, the part decreases that it was not fittable by deconvolution of the spectra. At 67 % RH, the trend is shifted to a lower temperature, and the maximum is reached at about 370 K.

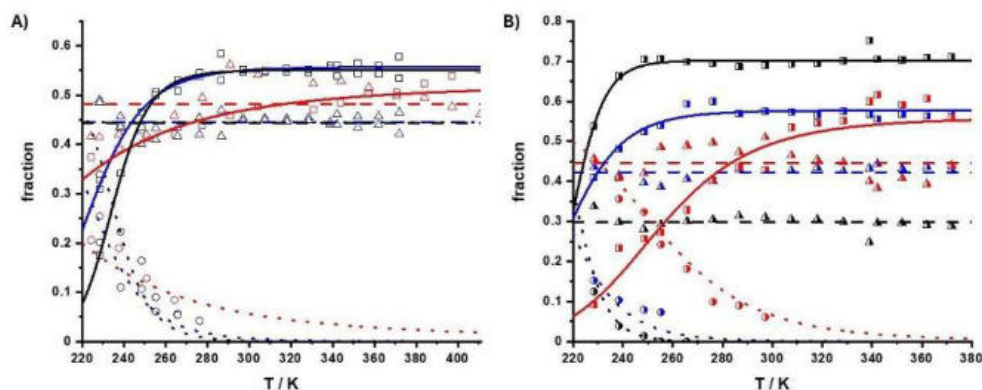


Figure 3: Calculated fraction of protons from the deconvoluted ^1H NMR spectrums (figures S1-6) for the adsorbed water in the mobile (squares) and immobile (circles) phase and the fraction of the protons of the frameworks (triangles) for SPAF-303_x ($x = 0.3$ (blue), 0.5 (red), and 0.8 (black)) at 33 % RH (A) and 67 % (B).

The appearance of the broad component indicates water molecules that are strongly bound to the network, more precisely to the sulfonic acid groups. These water molecules are immobile, whereas the narrow component shows mobile water in the pore. The mobile component grew in favor of the immobile one, with the share of the network remaining constant. The presence of these two components and their temperature dependence enables us to calculate the entropy ΔS° and enthalpy ΔH° for the increasing mobile water ratio $p(\text{H}_2\text{O}_{\text{mo}})$ by the following equation.

$$p(\text{H}_2\text{O}_{\text{mo}}) = \frac{1 - p_{\text{framework}}}{1 + e^{\Delta H^\circ/RT} \cdot e^{-\Delta S^\circ/R}} \quad (1)$$

$f_{\text{framework}}$ is the ratio of the protons of the framework and enables to calculate with $p(\text{H}_2\text{O}_{\text{mo}})$ the corresponding immobile proton ratio ($p(\text{H}_2\text{O}_{\text{im}})$).

$$p(\text{H}_2\text{O}_{\text{im}}) = 1 - p(\text{H}_2\text{O}_{\text{mo}}) - p_{\text{framework}} \quad (2)$$

The fitted ratios $p(\text{H}_2\text{O}_{\text{mo}})$ and $p(\text{H}_2\text{O}_{\text{im}})$ are shown in Figure 3 and the enthalpy and entropy are listed in Tab. 1. For every sulfonation degree and relative humidity, the immobile water species is preferred by 11 to 67 $\text{kJ mol}^{-1} \text{K}^{-1}$. Whereas the entropy is lower by 55 to 303 $\text{J mol}^{-1} \text{K}^{-1}$. For all sulfonation degrees, enthalpy and entropy are increasing with increasing humidity (33 to 67 % RH). Compared to 100 % RH the enthalpy and entropy for the sulfonation degrees of 0.3 and 0.8 at 33 and 67 % RH are about 1.5 to 2 times higher. This is caused by the strong interactions of water molecules and sulfonic acid groups. The relative amount of water molecules which are in strong interaction with the sulfonic acid groups are higher for lower humidities than for 100 % RH. For higher relative humidities than 67 % the multilayer

adsorption occurs and the frameworks start to swell. For the SPAF-303_{0.5} the enthalpy and entropy are rising with increasing humidity and reach their maximum at 100 % RH. SPAF-303_{0.5} has the lowest entropy and enthalpy of all sulfonation degrees. This trend can be explained by the homogeneous distribution of sulfonic acid groups in the framework and that every adsorbed water molecule experiences the same strong interaction in the pore volume.

Tab. 1: Fitted enthalpy in $\text{kJ mol}^{-1} \text{K}^{-1}$ and entropy in $\text{J mol}^{-1} \text{K}^{-1}$ for the mobile and immobile water component of SPAF-303_x displayed in Figure 2 with eq(1).

RH / %	SPAF-303 _{0.3}		SPAF-303 _{0.5}		SPAF-303 _{0.8}	
	ΔH°	ΔS°	ΔH°	ΔS°	ΔH°	ΔS°
33	33	147	11	55	52	225
67	37	168	20	79	67	303

Further investigations of the mobility of protons are made by observing the relaxation times of $\text{H}_2\text{O}@SPAF - 303_x^{\text{RH}}$. For all sulfonation degrees and relative humidities, the curves were simulated by a biexponential T_1 function (eq. (1), ESI) with stretching values b_1 and b_2 (Figures S6-S14, Tables S5-S10). The b value indicates a homogeneity distribution of proton spins, for b is equal one, and a second species whereas the b value is not equal one. These protons spins are heterogenous distributed to the magnetic field, that indicates an immobile species of protons. The two observed relaxation times with less than 1 s are in line with the suggestion that no ice water is formed in the pores (Figure 4A). For the sulfonation degrees of 0.3 and 0.8, the T_1 times are equal whereas for 0.5 the T_1 time is about half a decade shorter. For all sulfonation degrees, the relaxation time of the framework is temperature-independent. The T_1 relaxation times for the $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ are strongly temperature-dependent. The water and oxonium ions in SPAF-303_{0.3} have the longest relaxation time for both humidities and in SPAF-303_{0.5} the shortest one, especially at 67 % RH. The T_1 minima are at 315 K (SPAF - 303_{0.3}³³), 331 K (SPAF - 303_{0.3}⁶⁷), 320 K (SPAF - 303_{0.5}³³), 317 K (SPAF - 303_{0.5}⁶⁷), 308 K (SPAF - 303_{0.8}³³), and 295 K (SPAF - 303_{0.8}⁶⁷). The short spin-lattice relaxation times cannot be explained by a ^1H - ^1H dipolar coupling. Instead, it is caused in the same way as for the 100 % RH samples by the paramagnetic Pd and Fe centers with results in heteronuclear dipole interactions. These observations are in line with the exchange activation barriers of line shape analysis.

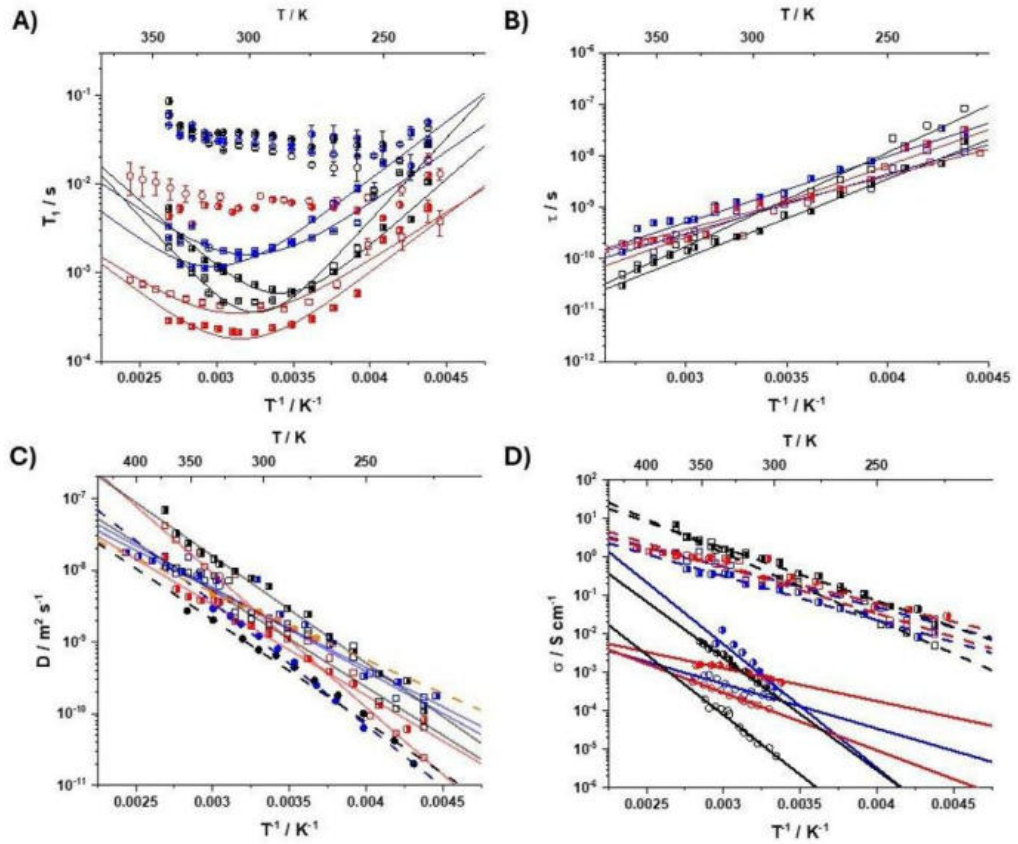


Figure 4: A) Arrhenius plot of T_1 times (sulfonation degrees of 0.3 blue, 0.5 red, and 0.8 black) simulated from magnetization recovery experiment (Figures S8-S13). Protons of the framework are represented by the circles and protons of water and oxonium ions are shown by squares. Data at 33 % RH are empty and half-filled for 67 % RH. The short T_1 time is fitted with a BPP-type function as a guide for the eye. B) Correlation times τ for the H_2O/H_3O^+ translation calculated from T_1 measurements with homonuclear coupling function of SPAF-303^{RH}. The color code is equal to A). C) Self-diffusion coefficients (squares) calculated from correlation times τ and an assumed mean distance $\langle r \rangle$ of 3.5 nm with the color code of A). the orange circles represents the diffusion data of water^[28] and the circles giving the diffusion data measured by SFG NMR experiments for SPAF-303¹⁰⁰_{0.3} and SPAF-303¹⁰⁰_{0.8}. D) Arrhenius-plot of the calculated conductivity with Nernst-Einstein relation, using the proton number density given in Tab. S11, from NMR (squares) and the conductivity from EIS measurements (circles), adapted from ref. 26. The color code follows the same as mentioned before. The lines (dashed for σ_s^{NMR} and solid for σ_s^{EIS}) are guides for the eye.

The presence of the paramagnetic centers and the heteronuclear dipole coupling between these centers and the protons of H_2O/H_3O^+ allows to calculate the short range translational motion of the mobile protons to the immobile paramagnetic centers according to the established method for SPAF-303_x with 100 % RH.^[26] Because of the complexity of the spectral density J of the heteronuclear dipole coupling, for the equation (3) the spectral density of a homonuclear dipole coupling with τ as correlation time was used..^[29–31]

$$\frac{1}{T_1} = C \cdot J(\omega, \tau) \quad (3)$$

$$J(\omega, \tau) = \frac{\tau}{1 + (2\omega\pi\tau)^2} \quad (4)$$

With the equation and the T_1 data from Figure 4A the correlation times τ were determined for every sample (Figure 4B). The rising correlation time with increasing temperatures indicates a thermal-activated process for the translational motion. With the underlying relation for self-diffusion coefficients D (eq. 5) can be calculated from the translational motion and the mean distance $\langle r \rangle$, which is assumed to be 3.5 nm equal as for the 100 % RH samples of SPAF-303_x.^[26]

$$D = \frac{\langle r \rangle^2}{6\tau_{trans}} \quad (5)$$

The diffusion coefficients are for the samples SPAF-303_{0.3} and SPAF-303_{0.5} are nearly independent of the water content of the sample and the sulfonation degree (Figure 4C). Moreover, D is in the same order as the diffusion coefficient for water. By using the Nernst-Einstein relation (eq. 6) the conductivity σ_x^{NMR} can be calculated. For the calculation the proton number density n_x is assumed to be equal as for the 100 % RH samples (Tables S11).

$$\sigma_x^{NMR} = \frac{n_x e^2 D}{k_B T} \quad (6)$$

The calculated conductivities by NMR (Figure 4D) give a short-range translation motion of water and oxonium molecules (< 10 nm) which represent the diffusion for local pores. These short-range motions are in the same order as for the 100 % RH sample.^[26] The local motions of the guest molecules are independent of the sulfonation degree and the relative humidity. The predicted conductivities σ_x^{NMR} calculated from relaxation data by NMR do not match them measured by impedance measurements (Figure 4D). The differences between σ_x^{NMR} and σ_x^{EIS} are about 3 to 5 orders of magnitude. These deviations indicate that the Nernst-Einstein-equation does not apply anymore, because the free diffusion of molecules through the frameworks is not possible anymore at 33 % RH and 67 % RH.^[32] The frameworks are partially filled with water. This partially filled pores lead to a collapse structure of the framework. This state leads to an allowed motion of guest molecules in the pore but not between the pores, so the pores are not connected to each other. This behavior is known as bottleneck structure which limits a long-range diffusion.^[33]

The underlying conduction mechanism of the frameworks SPAF-303_x at 33 % RH and 67 % RH can be explained by the T_1 measurements, the activation energies of EIS and NMR compared with the conductivity measured and predicted for both methods. $H_2O@SPAF-303_x$ gives always two spin-lattice relaxation times, whereas one T_1 component is referred to the guest molecules. The SP ^1H NMR measurements gave two species of water and oxonium molecules inside the framework. This reinforces the thesis put forward by SPAF-303_x at 100 % RH that there are two water regimes that are in exchange with each other.^[26] Likewise at 100 % RH, SPAF-303_x shows for lower relative humidities the same temperature dependance of about 20 kJ mol⁻¹ (Tab. 2). The activation barriers $E_{A \text{ diffusion}}$ for SPAF-303_x at 33 % RH and 67 % RH are lower or equal compared to $E_{A \text{ EIS}}$ which affirmed the thesis that the macroscopic conductivity is not primarily determined by the free diffusion of oxonium ions. In addition to the aforementioned bottleneck structure, σ_x^{EIS} is also determined by the strong interaction in the confinement between the SO_3^- -groups and the oxonium ions. This is given by the activation energies of the exchange $E_{A \text{ exchange}}$ which are in the same order as the activation energy measured by impedance spectroscopy. Moreover, the arrangement of the sulfonic acid groups at SPAF-303_{0.5}^[26] gives the best surface structuring inside the pores. The observed alternating arrangement of the sulfonic acid groups leads to a reduced activation energy for diffusion, exchange and conductivity (Tab. 2) compared to the sulfonation degree of 30 and 80 %.

Tab. 2: Activation barrier $E_{A \text{ diffusion}}$ of SPAF-303 calculated from σ_x^{NMR} (Figure 4D) in kJ mol⁻¹. Additionally, the activation barrier $E_{A \text{ exchange}}$ and $E_{A \text{ EIS}}$ ^[26] in kJ mol⁻¹ added for comparison the proton diffusion of NMR and EIS measurements.

Framework	Relative humidity					
	33 % RH			67 % RH		
	$E_{A \text{ diffusion}}$	$E_{A \text{ exchange}}$	$E_{A \text{ EIS}}$	$E_{A \text{ diffusion}}$	$E_{A \text{ exchange}}$	$E_{A \text{ EIS}}$
SPAF-303 _{0.3}	20	33	23	22	37	49
SPAF-303 _{0.5}	18	11	29	23	20	15
SPAF-303 _{0.8}	33	52	57	26	67	54

Conclusion

In conclusion, this study provides detailed insights into the technic of determining the proton conduction mechanisms and water confinement depending on sulfonation degree and relative humidity in SPAF-303 frameworks. It was possible by combination of impedance measurement with NMR spectroscopy technics to highlight the importance of confinement, structuring of pore space and framework as well as the influence of water content on the proton conductivity of SPAF-303_x.

The results showed that the aspect of lower water contents in the frameworks influence the macroscopic conductivity by hindering the connection of the pores to each other by about 4 orders of magnitude compared to the promised conductivity by Nernst-Einstein equation (1 S cm^{-1}). The diffusion coefficients of SPAF-303_x at 33 and 67 % RH, about $10^{-9} \text{ m}^2 \text{ s}^{-1}$, are in the same order as for the 100 % RH sample and as water. This high diffusivity can be explained by the pore structure of the frameworks despite the strong confinement. This strong confinement prefers to build up two subensembles of water inside the pore. One is an immobile which is in strong interaction with the sulfonic acid groups and a mobile species inside the pores. These subensembles are in continuous exchange between each other with favor to the mobile species with increasing temperature. As determined by the activation energies of the subensembles it is known that for the both relative humidities oxonium ions and water molecules are always in contact with the sulfonic acid groups whereas at 100 % RH SPAF-303_{0.5} enables that oxonium ions are placed in the mobile regime only. This exchange of the two regimes significantly influences the conductivities in the frameworks, in addition to the bottleneck effect.

By the study of the three frameworks at 33 % RH and 67 % RH we have demonstrated the further use of the combination of impedance and NMR spectroscopy in paramagnetic systems with short relaxation times. In addition to the formation of strong confinement, which has a larger influence than the charge carrier concentration, we have shown that the water content has a decisive influence on the conductivity. This knowledge will help to study further frameworks for their conduction mechanism and to engineer new systems with their operating conditions for aqueous proton conduction in the future.

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Supporting Information

Understanding of Proton Conduction in Confinement of SPAF-303

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Synthesis and Characterization of the frameworks

The synthesis and characterization were done according to and adapted to the protocol of Winterstein et al.^[1]

SPAF-2

The framework PAF-2 (120 mg) was placed in a frit with an flask at the bottom. The volume of this setup was degassed and placed under argon atmosphere. Fuming sulfonic acid was placed in the flask and the setup was set for a defined time (30, 60, 90 s) under reduced pressure. After the time for sulfonation the plug was open to argon and the gas was led through the sample. Afterwards the framework was purified by ethanol Soxhlet. The framework was dried under reduced pressure at 120 °C. The yields were 139.4 mg ($x = 0.3$), 161.8 mg ($x = 0.5$), and 192.4 mg ($x = 0.8$) corresponding to 0.23 mmol (91 %), 0.24 mmol (94 %), and 0.22 mmol (87 %).

Tab. S 1: Titration of SPAF-303 to determine the degree of sulfonation.

	$M_{\text{SPAF-303}} / \text{mg}$	$V_{\text{NaOH}} / \text{ml}$	sulfonation degree after washing / %	IEC / meq g ⁻¹
<i>SPAF-303_{0.3}</i>	10.7	2.967	30	2.77
<i>SPAF-303_{0.5}</i>	10.3	4.242	50	4.12
<i>SPAF-303_{0.8}</i>	10.0	5.630	80	5.63

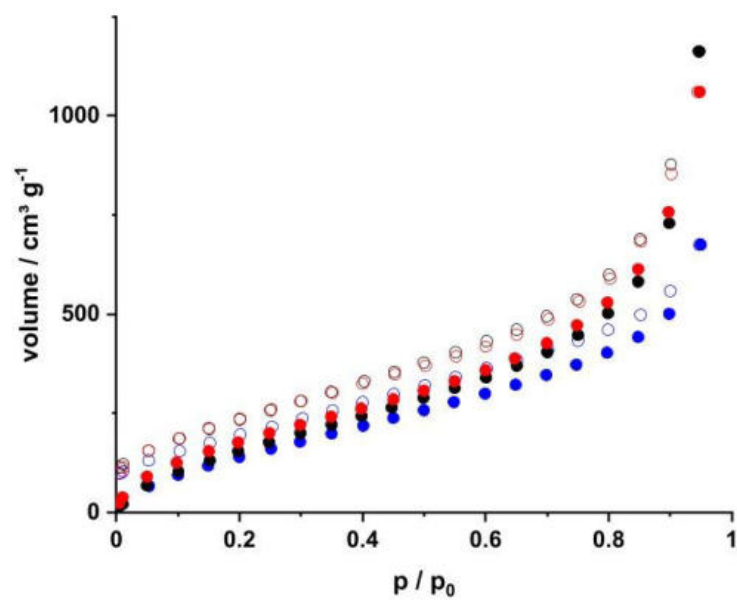


Figure S 1: Water physisorption measurement of SPAF-303_x (blue 30 %, red 50 %, and black 80 %) at 293 K.

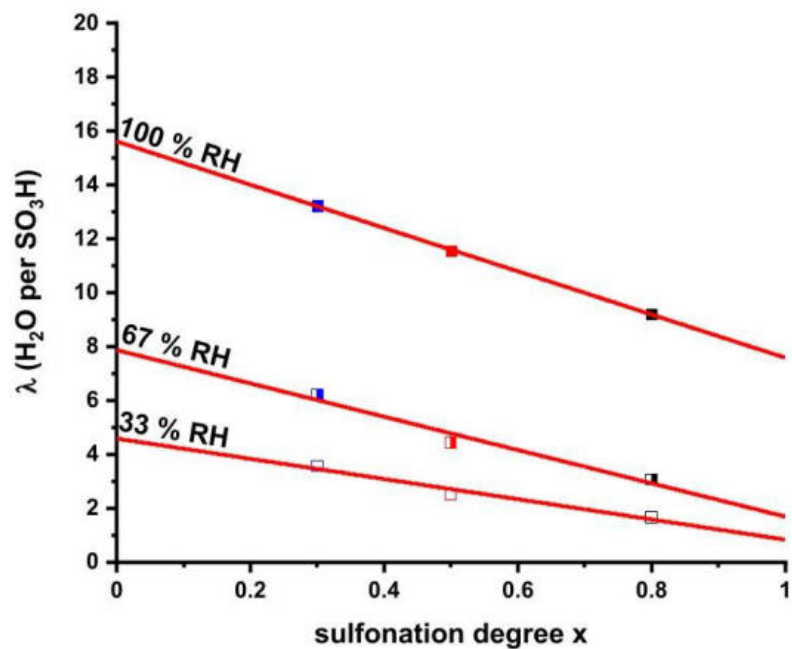


Figure S 2: Number of H₂O per SO₃H group (λ) determined from the water isotherms (Figure S 1) at 33, 67, and 100% RH for SPAF-303_x ($x=0.3$ blue, $x=0.5$ red, and $x=0.8$ black).

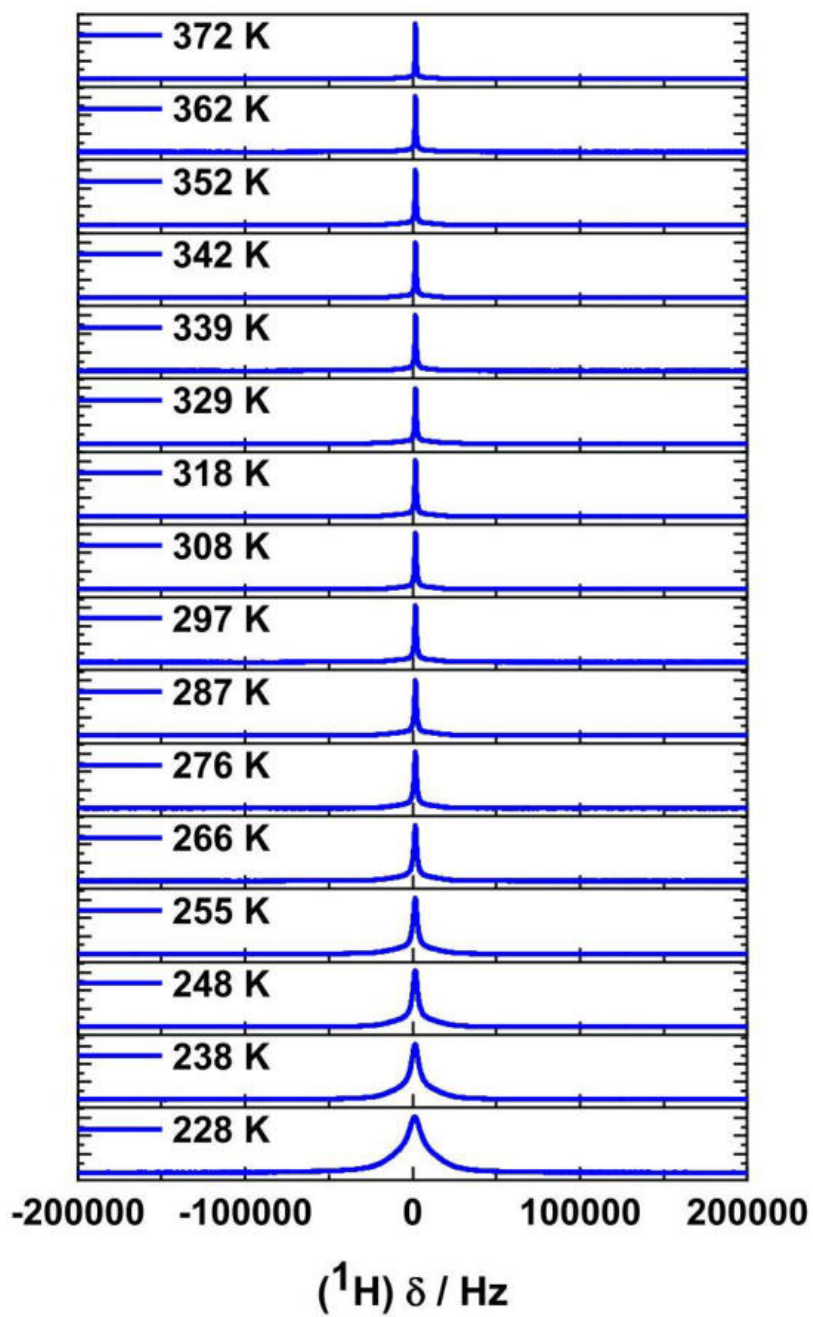


Figure S 3: Wideline ^1H single pulse NMR spectra of SPAF-303_{0.3} at 33 % RH.

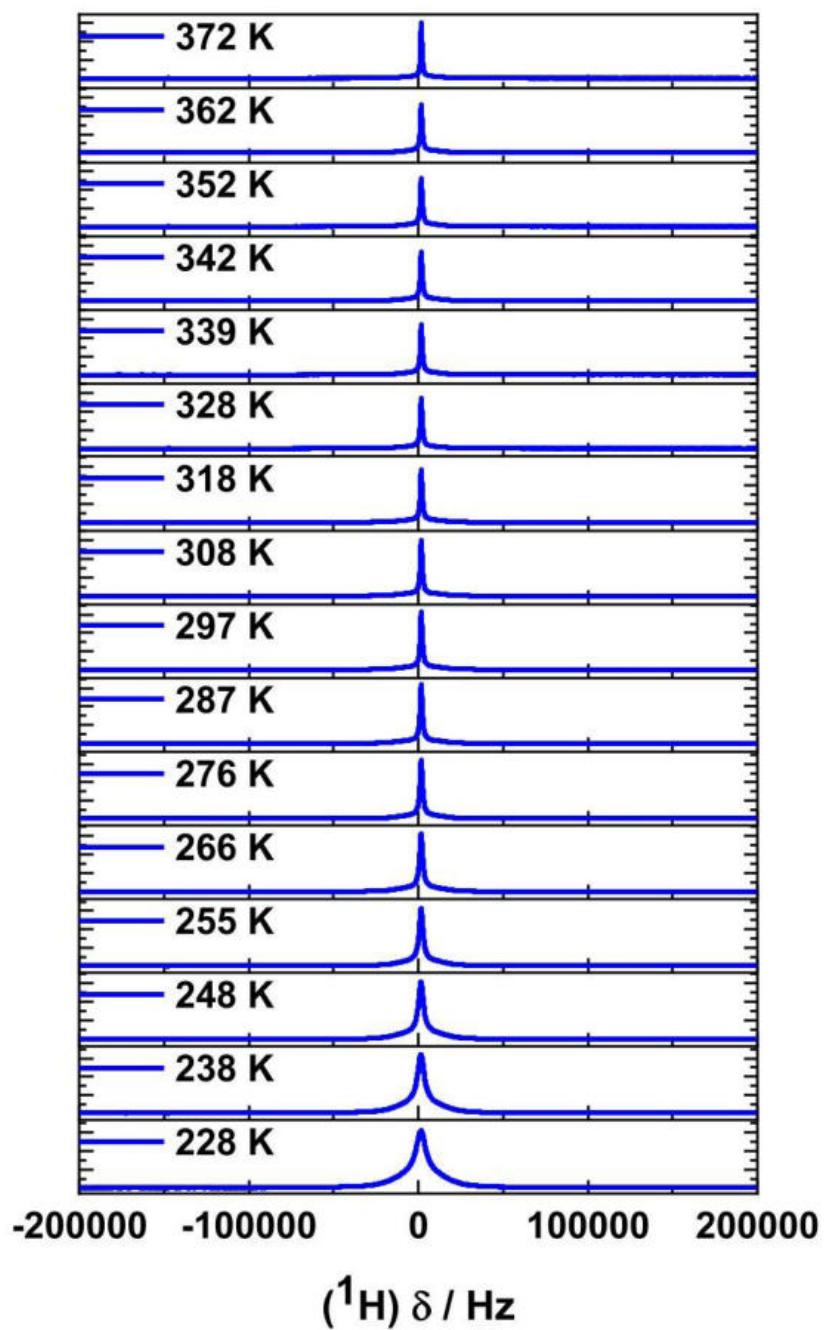


Figure S 4: Wideline ^1H single pulse NMR spectra of SPAF-303_{0.3} at 67 % RH.

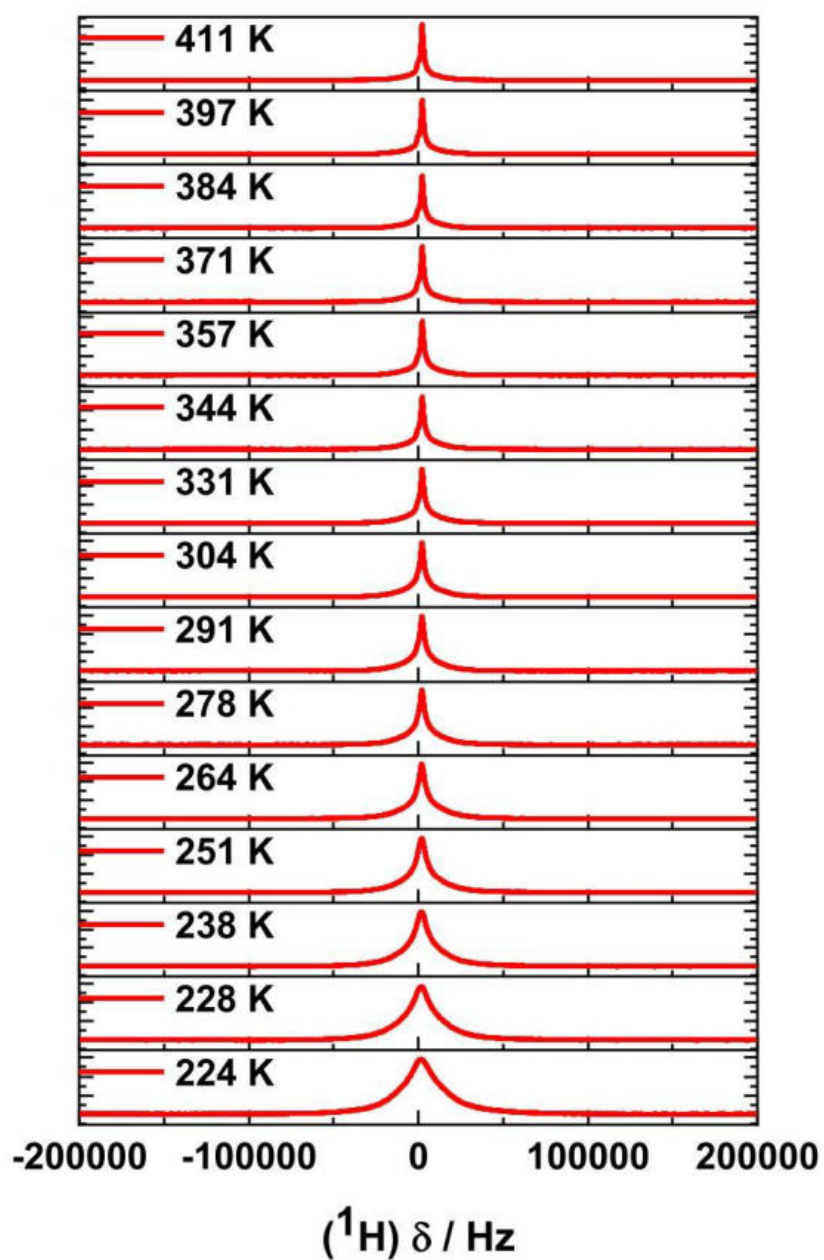


Figure S 5: Wideline ^1H single pulse spectra of SPAF-303_{0.5} at 33 % RH.

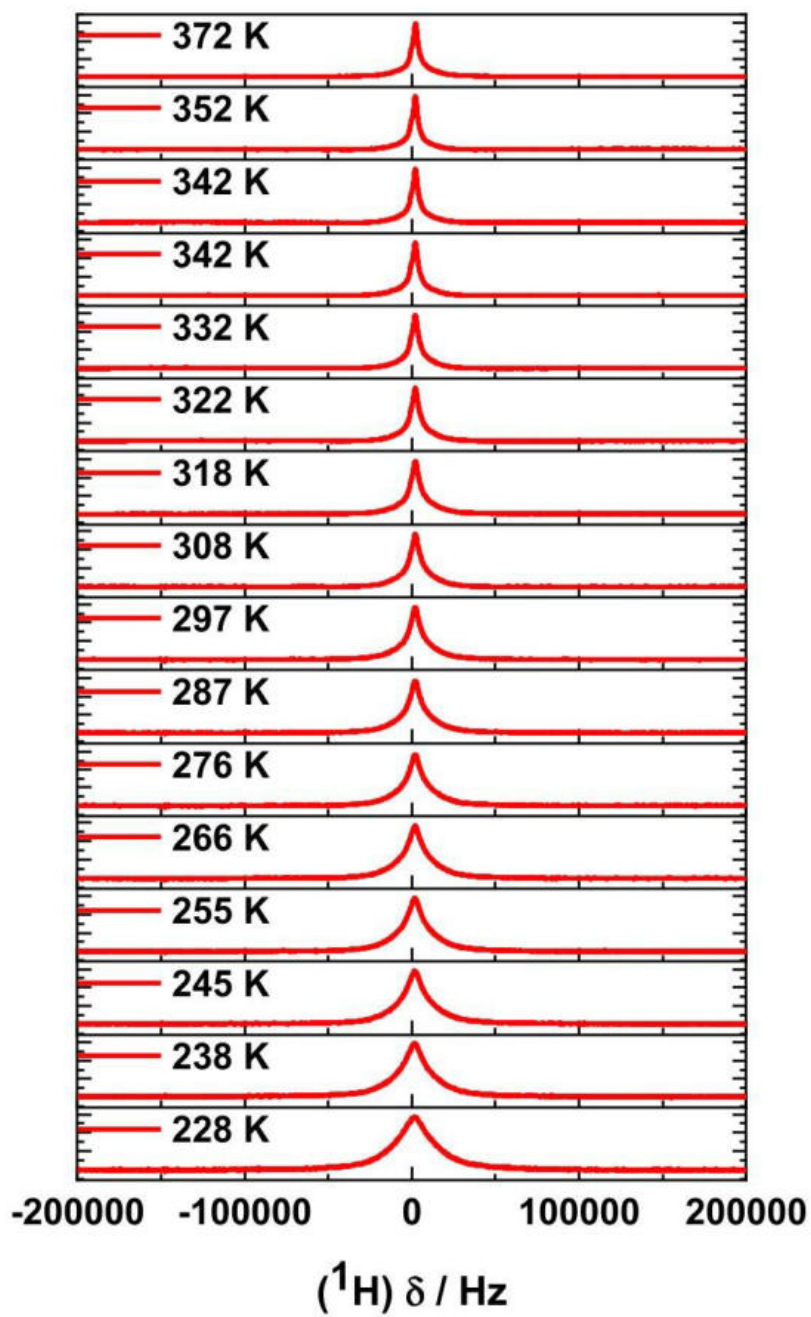


Figure S 6: Wideline ^1H single pulse NMR spectra of SPAF-303 at 67 % RH.

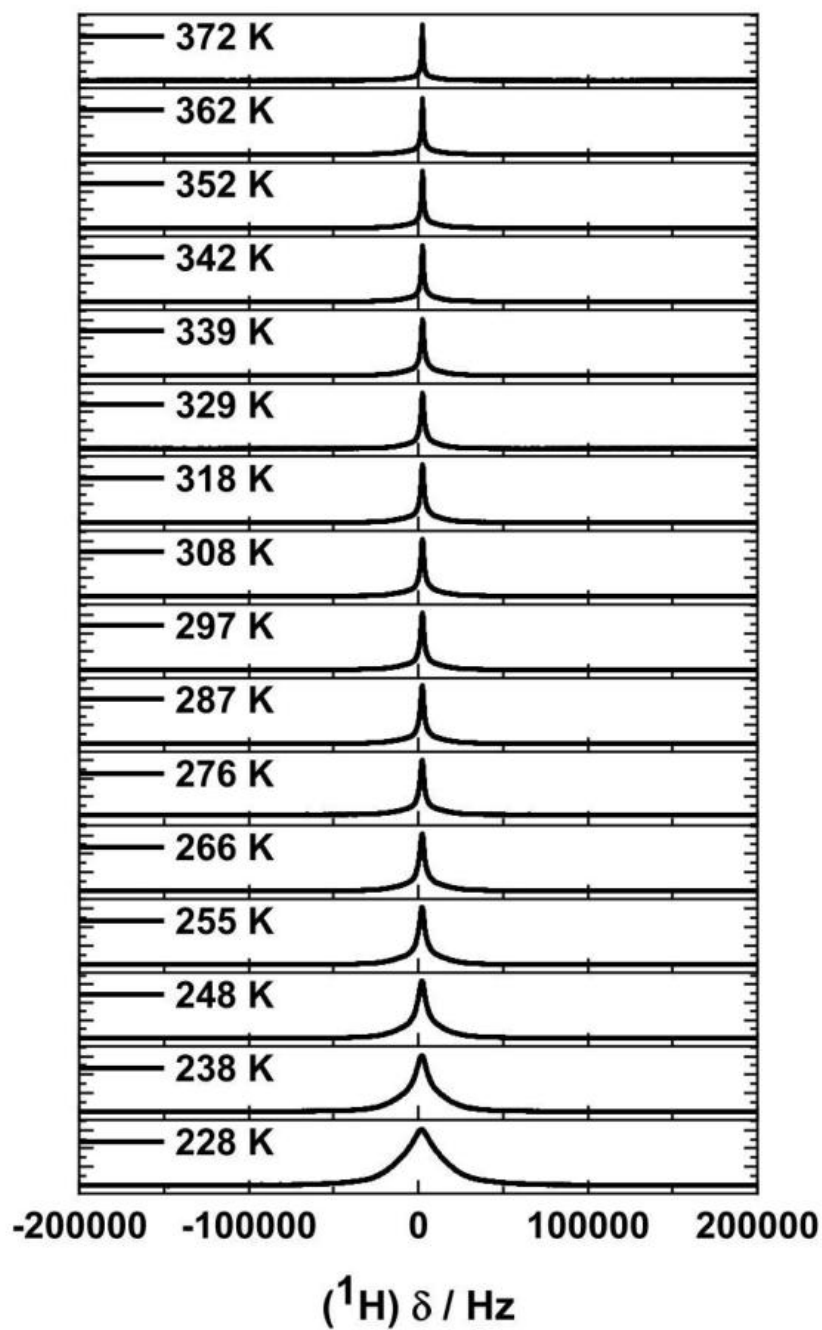


Figure S 7: Wideline ^1H single NMR pulse spectra of SPAF-303_{0.8} at 33 % RH.

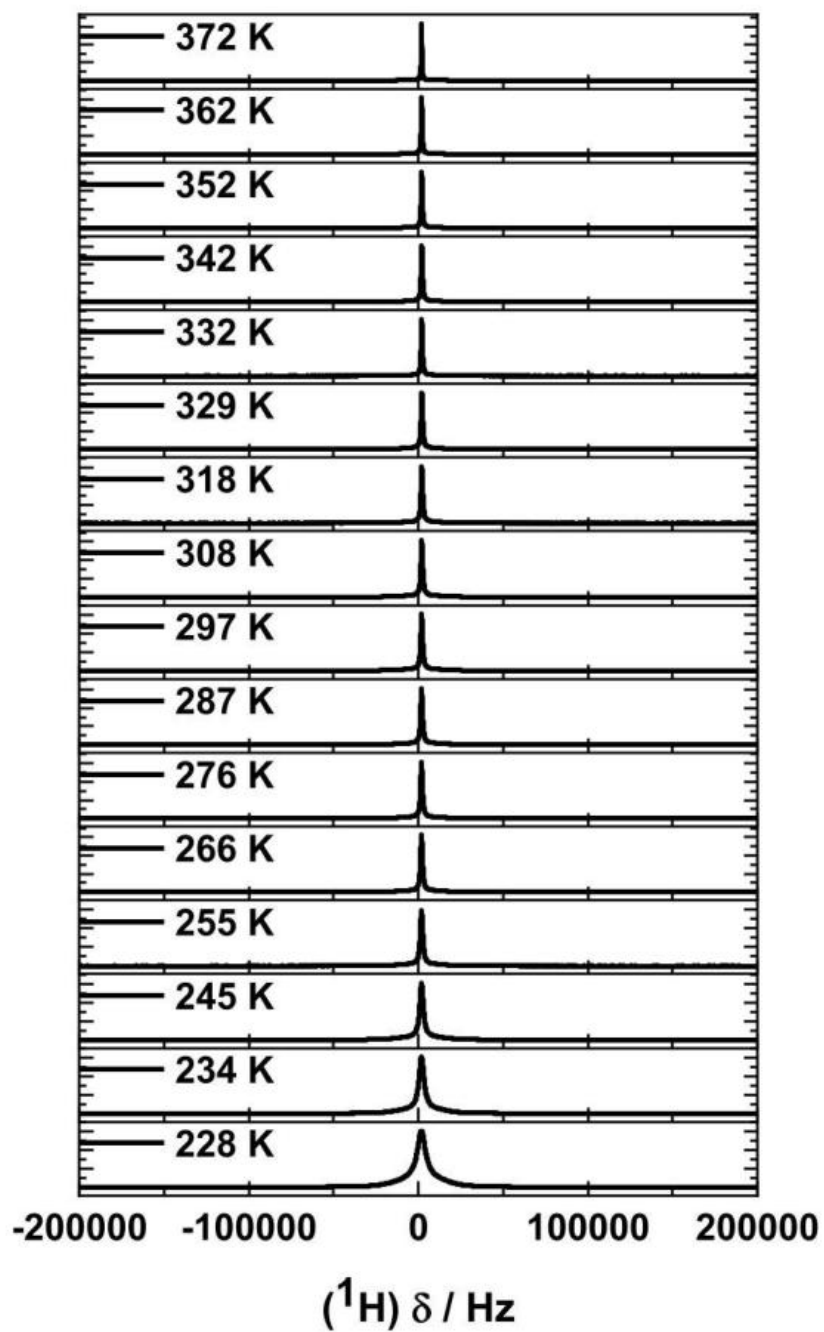


Figure S 8: Wideline ^1H single pulse NMR spectra of SPAF-303_{0.8} at 67 % RH.

Understanding of Proton Conduction in Confinement of SPAF-303

Tab. S 2: Temperature-dependent trend of full width of half maximum (fwhm) of ^1H SP NMR spectra of SPAF-303_x at 33 % RH (Figures S1, S3, S5). The fwhm were determined by deconvolution of the spectra with two Gaussian and one Lorentzian profile.

SPAF-303 _{0.3}				SPAF-303 _{0.5}				SPAF-303 _{0.8}			
T / K	Fwhm mobile / Hz	Fwhm immobile / Hz	fwhm framework / Hz	T / K	Fwhm mobile / Hz	Fwhm immobile / Hz	fwhm framework / Hz	T / K	Fwhm mobile / Hz	Fwhm immobile / Hz	fwhm framework / Hz
228	7752	78591	28990	224	11169	70078	29571	228	10106	73698	29905
238	5028	79591	28989	228	9830	65624	29863	238	7207	65457	28211
248	3282	80591	26990	238	7513	66883	28729	248	5399	61358	26966
255	2823	78591	28990	251	5933	66118	27553	255	4244	71595	28000
266	2150	77056	27334	264	4912	62144	27349	266	3633	74296	28001
276	1721	78938	27184	278	4320	73246	27696	276	3123		30343
287	1450		27045	291	4084	55754	27256	287	2830		28444
297	1292		26963	304	3840		27982	297	2723		27522
308	1217		26383	331	3107		28699	308	2653		27232
318	1136		25661	344	2999		27967	318	2574		26165
329	1078		25155	357	2312		27014	328	2501		25625
339	1043		25026	371	2642		26036	339	2421		25176
342	1007		24699	384	2543		25596	342	1876		24268
352	960		24263	397	2424		25085	352	1740		23463
362	858		24191	411	2342		26072	362	1564		22440
372	706		24122					372	1279		21145

Tab. S 3: Temperature-dependent trend of full width of half maximum (fwhm) of ^1H SP NMR spectra of SPAF-303_x at 67 % RH (Figures S2, S4, S6). The fwhm were determined by deconvolution of the spectra with two Gaussian and one Lorentzian profile.

SPAF-303 _{0.3}				SPAF-303 _{0.5}				SPAF-303 _{0.8}			
T / K	Fwhm mobile / Hz	Fwhm immobile / Hz	fwhm framework / Hz	T / K	Fwhm mobile / Hz	Fwhm immobile / Hz	fwhm framework / Hz	T / K	Fwhm mobile / Hz	Fwhm immobile / Hz	fwhm framework / Hz
228	6409	73886	28233	228	8156	75339	24999	228	5582	73417	26648
238	4559	73886	27847	238	8948	75338	25599	238	3460	76424	29537
248	3366	73887	27245	248	8140	75339	24999	248	2486	72424	30537
255	2603	73885	26911	255	7338	75337	24999	259	1661	60250	29105
266	2115	73886	26692	266	7477	75339	26869	269	1310		28110
276	1747	78886	26512	276	7561	76339	28549	276	1230		27511
287	1525		26938	287	7149	76339	28549	287	1230		26406
297	1419		26135	297	6334	78338	26987	293	1246		26266
308	1345		2633	306	6115		26764	297	1228		25947
318	1312		25562	318	5367		23591	308	1176		25434
329	1329		25170	329	4826		23846	318	1080		25397
339	1326		24831	339	4863		24683	332	781		23710
342	1319		24037	342	4405		23256	342	954		24278
352	1313		24162	352	4005		22663	352	799		23846
362	1234		23653	362	3784		22373	362	678		23235
371	955		23464					372	489		22614

Tab. S 4: Calculated and measured ratios of protons from water and oxonium ions to protons of the framework of SPAF-303_v.

<i>RH</i> / %	<i>SPAF-303</i> _{0.3}	<i>SPAF-303</i> _{0.5}	<i>SPAF-303</i> _{0.8}
33	0.40/0.44	0.45/0.50	0.52/0.57
67	0.52/0.48	0.58/0.59	0.64/0.72

Spin-Spin relaxation

The evaluation of the inversion recovery build-up curves to determine the T^1 relaxation time was done with equation (1). M_0 is giving the total magnetization, I the ratio of the first component, A_x ratio of the magnetization, and T_x the T^1 relaxation time of the corresponding species. b_x defines the stretching factor, which displays the homogenization of the spin orientation to the magnetic field of each species, whereas b_1 is fixed to 1 for all fittings.

$$M(t) = M_0 \left(I \left(1 - A_1 e^{-\left(\frac{t}{T_1}\right)^{b_1}} \right) + (1 - I) \left(1 - A_2 e^{-\left(\frac{t}{T_2}\right)^{b_2}} \right) \right) \quad (1)$$

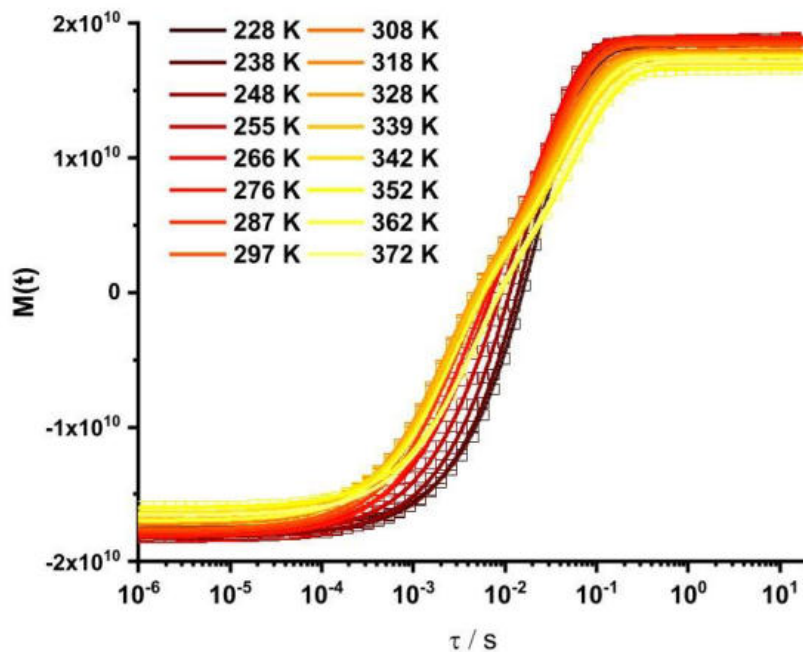


Figure S 9: ^1H spin-lattice relaxation build-up curves of SPAF – $303_{0.3}^{33}$ acquired with an inversion sequence.

Tab. S 5: Fitting parameters of the SPAF – $303_{0.3}^{33}$ build-up curves Figure S 9.

T	M_0	I	A_1	T_1	A_2	T_2	b_1	b_2
228	1.84E+10	0.44	2.00	0.01834	1.92	0.03218	1.00	0.84
238	1.87E+10	0.55	2.00	0.01843	1.92	0.02792	1.00	0.76
248	1.89E+10	0.13	2.00	0.00844	1.96	0.02079	1.00	0.83
255	1.89E+10	0.18	1.78	0.00366	2.00	0.02050	1.00	0.84
266	1.89E+10	0.25	1.85	0.00295	2.00	0.02139	1.00	0.82
276	1.89E+10	0.29	1.88	0.00246	2.00	0.02257	1.00	0.77
287	1.86E+10	0.33	1.88	0.00211	2.00	0.02445	1.00	0.76
297	1.84E+10	0.36	1.89	0.00190	2.00	0.02647	1.00	0.76
308	1.80E+10	0.38	1.89	0.00176	2.00	0.02843	1.00	0.75
318	1.77E+10	0.39	1.89	0.00173	2.00	0.03074	1.00	0.74
328	1.78E+10	0.39	1.89	0.00176	2.00	0.03233	1.00	0.74
339	1.77E+10	0.39	1.89	0.00191	2.00	0.03497	1.00	0.73
342	1.70E+10	0.38	1.90	0.00217	2.00	0.03794	1.00	0.72
352	1.67E+10	0.35	1.88	0.00334	2.00	0.04652	1.00	0.72
362	1.75E+10	0.38	1.92	0.00218	2.00	0.03736	1.00	0.71
372	1.72E+10	0.36	1.90	0.00335	2.00	0.04580	1.00	0.71

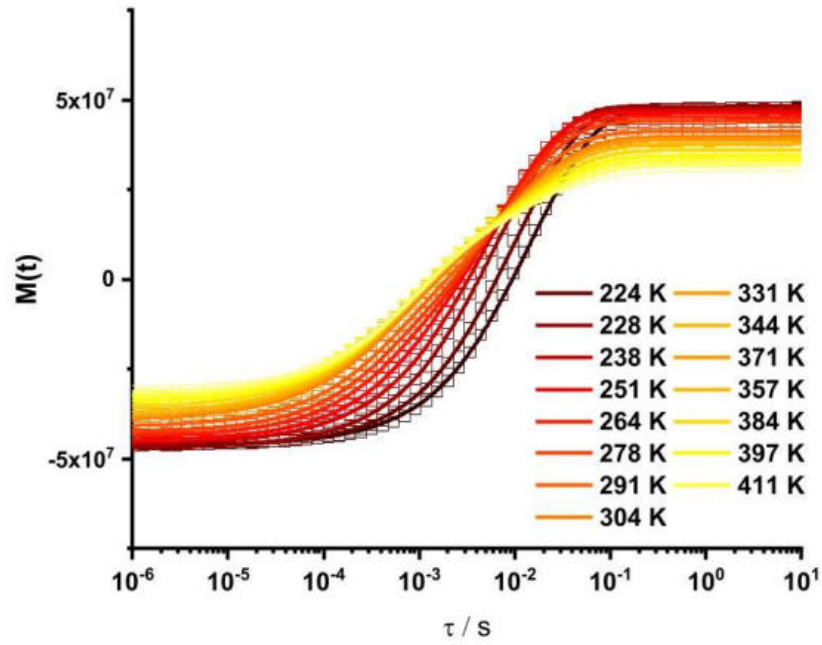


Figure S 10: ^1H spin-lattice relaxation build-up curves of SPAF – $303_{0.5}^{33}$ acquired with an inversion sequence.

Tab. S 6: Fitting parameters of the SPAF – $303_{0.5}^{33}$ build-up curves Figure S 10.

T	M_0	I	A_1	T_1	A_2	T_2	b_1	b_2
228	4.74E7	0.10	2.00	0.00569	1.96	0.0207	1.00	0.72
224	4.80E7	0.10	2.00	0.00382	1.97	0.0130	1.00	0.71
238	4.82E7	0.10	2.00	0.00249	1.97	0.0086	1.00	0.68
251	4.68E7	0.10	2.00	0.00179	1.98	0.0069	1.00	0.66
264	4.64E7	0.11	1.72	0.00073	2.00	0.0064	1.00	0.64
278	4.53E7	0.12	1.75	0.00047	2.00	0.0064	1.00	0.61
291	4.41E7	0.14	1.81	0.00039	2.00	0.0066	1.00	0.58
304	4.10E7	0.15	2.00	0.00038	2.00	0.0063	1.00	0.55
331	3.97E7	0.17	1.99	0.00039	2.00	0.0061	1.00	0.49
344	3.89E7	0.18	2.00	0.00042	2.00	0.0060	1.00	0.48
357	3.77E7	0.19	2.00	0.00045	2.00	0.0059	1.00	0.47
371	3.61E7	0.23	2.00	0.00047	2.00	0.0064	1.00	0.48
384	3.45E7	0.26	2.00	0.00053	2.00	0.0067	1.00	0.49
397	3.33E7	0.27	2.00	0.00059	2.00	0.0069	1.00	0.48
411	3.19E7	0.30	2.00	0.00066	2.00	0.0074	1.00	0.48

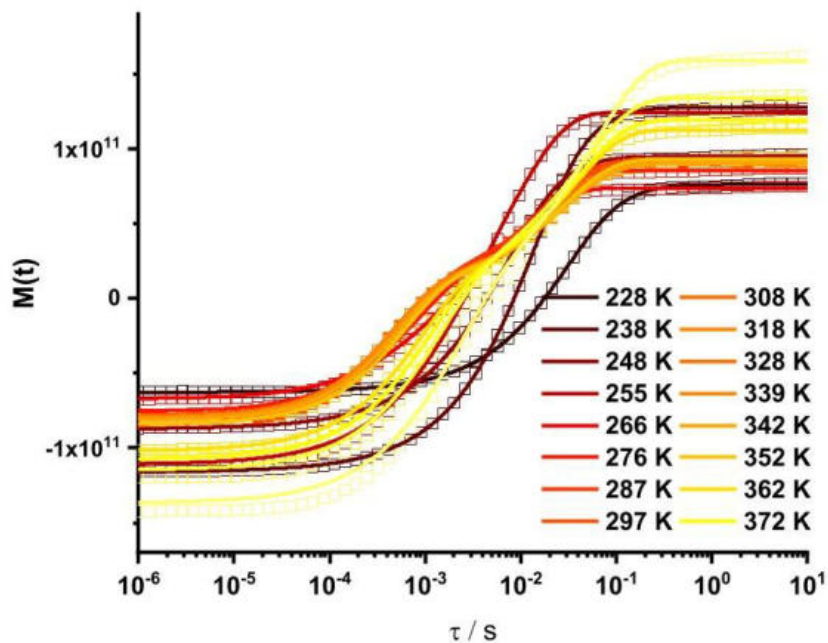


Figure S 11: ^1H spin-lattice relaxation build-up curves of SPAF – $303_{0.8}^{33}$ acquired with an inversion sequence.

Tab. S 7: Fitting parameters of the SPAF – $303_{0.8}^{33}$ build-up curves Figure S 11.

T	M_0	I	A_1	T_1	A_2	T_2	b_1	b_2
228	7.61E+10	0.51	1.67	0.0281	2.00	0.04246	1.00	0.64
238	1.28E+11	0.56	1.85	0.01329	2.00	0.01838	1.00	0.57
248	9.51E+10	0.60	1.89	0.00744	2.00	0.00845	1.00	0.49
255	1.24E+11	0.59	1.81	0.00189	2.00	0.01528	1.00	1.00
266	7.38E+10	0.58	1.81	0.00119	2.00	0.01514	1.00	1.00
276	8.56E+10	0.55	1.81	7.33E-04	2.00	0.01641	1.00	1.00
287	9.12E+10	0.58	1.78	5.80E-04	2.00	0.02051	1.00	1.00
297	9.30E+10	0.55	1.81	4.89E-04	2.00	0.02311	1.00	0.95
308	9.16E+10	0.55	1.79	4.66E-04	2.00	0.02526	1.00	0.89
318	9.04E+10	0.55	1.78	4.84E-04	2.00	0.02684	1.00	0.87
328	9.02E+10	0.48	1.84	4.68E-04	1.94	0.02376	1.00	0.72
339	9.31E+10	0.55	1.81	5.85E-04	2.00	0.02847	1.00	0.87
342	1.12E+11	0.55	1.80	8.70E-04	2.00	0.03578	1.00	0.92
352	1.19E+11	0.54	1.79	9.90E-04	2.00	0.03739	1.00	0.89
362	1.34E+11	0.54	1.75	0.00127	2.00	0.04381	1.00	0.89
372	1.59E+11	0.53	1.74	0.00196	2.00	0.06128	1.00	0.96

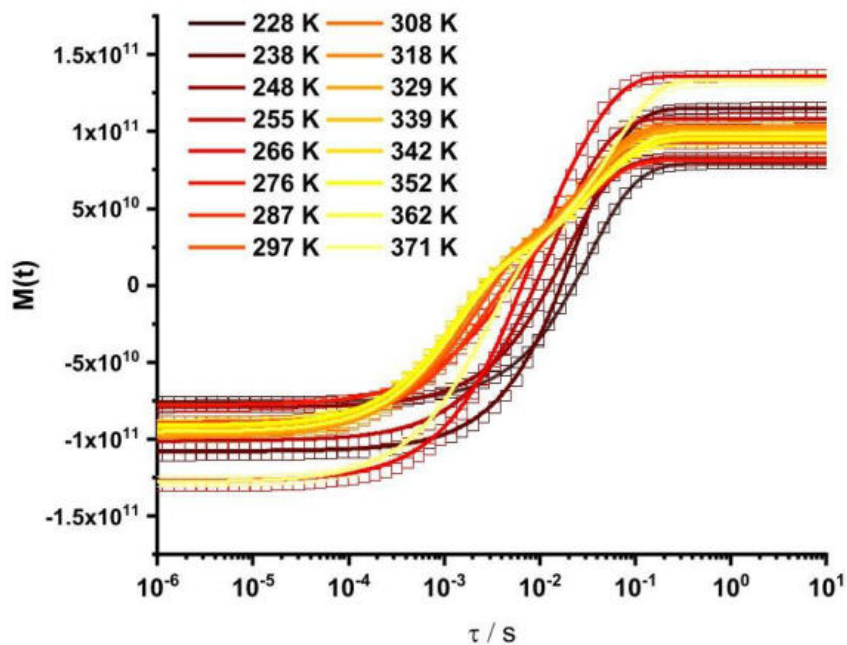


Figure S 12: ^1H spin-lattice relaxation build-up curves of SPAF – 303_{0.3}⁶⁷ acquired with an inversion sequence.

Tab. S 8: Fitting parameters of the SPAF – 303_{0.3}⁶⁷ build-up curves Figure S 12.

T	M_0	I	A_1	T_1	A_2	T_2	b_1	b_2
228	7.95E+10	0.56	2.00	0.02758	1.90	0.04983	1.00	0.88
234	1.15E+11	0.58	1.90	0.03801	2.00	0.01608	1.00	0.96
245	8.30E+10	0.60	1.93	0.01726	2.00	0.02497	1.00	0.78
255	1.09E+11	0.61	1.92	0.00893	2.00	0.0326	1.00	1.00
266	1.36E+11	0.62	1.91	0.00600	2.00	0.03434	1.00	1.00
276	8.16E+10	0.62	1.91	0.00401	2.00	0.03655	1.00	1.00
287	9.26E+10	0.50	1.94	0.00225	1.98	0.02779	1.00	0.92
297	9.99E+10	0.57	1.89	0.00195	2.00	0.03366	1.00	1.00
308	1.03E+11	0.57	1.90	0.00164	2.00	0.03472	1.00	1.00
318	1.03E+11	0.57	1.91	0.00148	2.00	0.0368	1.00	1.00
328	1.01E+11	0.47	1.91	0.00115	2.00	0.02906	1.00	0.78
332	9.68E+10	0.48	1.90	0.00114	2.00	0.03046	1.00	0.78
342	9.51E+10	0.48	1.91	0.00113	2.00	0.03147	1.00	0.77
352	9.50E+10	0.49	1.90	0.00116	2.00	0.03293	1.00	0.77
362	9.92E+10	0.48	1.90	0.00125	2.00	0.03477	1.00	0.76
372	1.33E+11	0.55	1.91	0.00245	2.00	0.05900	1.00	1.00

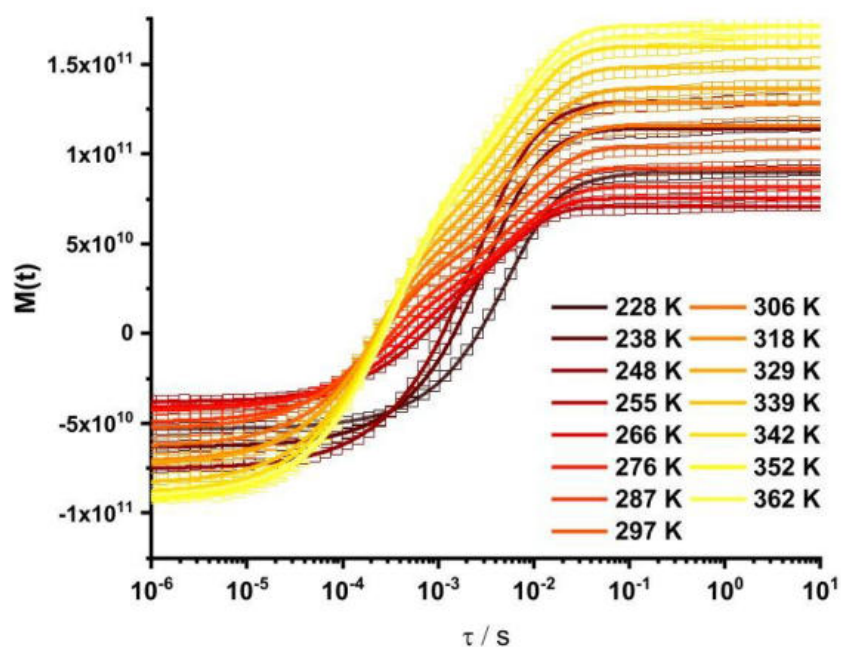


Figure S 13: ^1H spin-lattice relaxation build-up curves of SPAF – 303_{0.5}⁶⁷ acquired with an inversion sequence.

Tab. S 9: Fitting parameters of the SPAF – 303_{0.5}⁶⁷ build-up curves Figure S 13.

T	M_0	I	A_1	T_1	A_2	T_2	b_1	b_2
228	8.99E+10	0.60	2.00	0.0055	0.99	0.01258	1.00	0.56
239	1.14E+11	0.54	1.57	0.00299	1.54	0.00583	1.00	0.69
245	1.29E+11	0.58	1.29	0.00236	2.00	0.00412	1.00	0.62
255	7.03E+10	0.51	1.08	5.85E-04	2.00	0.00507	1.00	0.90
266	7.50E+10	0.51	1.09	4.03E-04	2.00	0.00546	1.00	0.82
276	8.16E+10	0.50	1.04	3.02E-04	2.00	0.00553	1.00	0.71
287	9.22E+10	0.53	1.11	2.59E-04	2.00	0.00617	1.00	0.70
297	1.04E+11	0.57	1.16	2.41E-04	2.00	0.00667	1.00	0.72
308	1.16E+11	0.53	1.13	2.12E-04	2.00	0.00539	1.00	0.63
318	1.28E+11	0.55	1.18	2.11E-04	2.00	0.00534	1.00	0.64
323	1.36E+11	0.55	1.15	2.15E-04	2.00	0.00482	1.00	0.61
332	1.48E+11	0.60	1.25	2.35E-04	2.00	0.00561	1.00	0.71
342	1.59E+11	0.62	1.26	2.54E-04	2.00	0.00578	1.00	0.74
352	1.66E+11	0.50	1.14	2.49E-04	2.00	0.00354	1.00	0.56
362	1.71E+11	0.61	1.24	2.87E-04	2.00	0.00531	1.00	0.72
372	1.65E+11	0.56	1.18	2.88E-04	2.00	0.00436	1.00	0.64

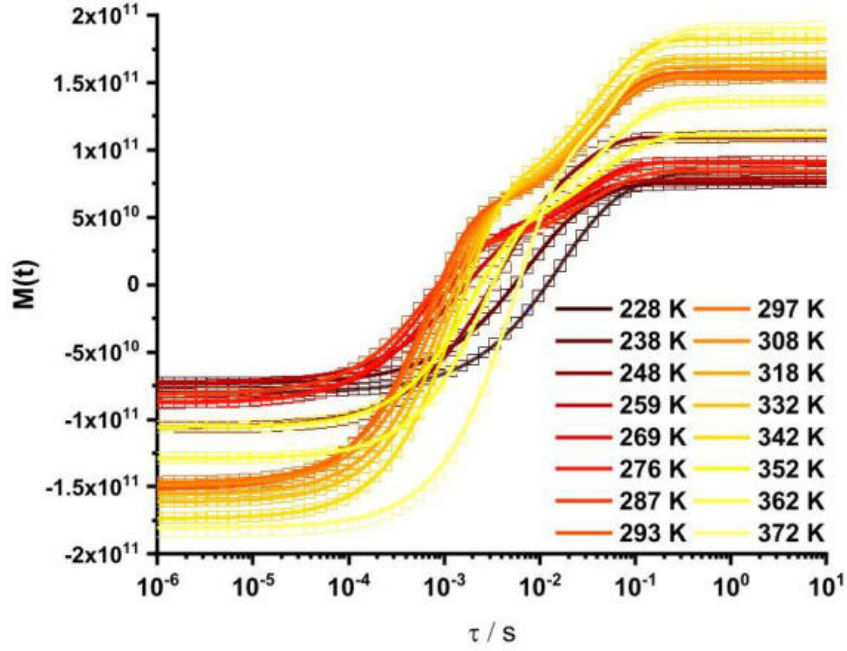


Figure S 14: ^1H spin-lattice relaxation build-up curves of SPAF – $303_{0.8}^{67}$ acquired with an inversion sequence.

Tab. S 10: Fitting parameters of the SPAF – $303_{0.8}^{67}$ build-up curves Figure S 14.

T	M_0	I	A_1	T_1	A_2	T_2	b_1	b_2
228	8.33E+10	0.33	1.90	0.01055	1.99	0.02949	1.00	0.72
234	7.53E+10	0.28	1.94	0.00401	1.99	0.01323	1.00	0.74
245	1.10E+11	0.72	1.93	0.00323	2.00	0.02792	1.00	1.00
255	7.75E+10	0.71	1.93	0.00161	2.00	0.02729	1.00	1.00
266	9.07E+10	0.70	1.93	0.00104	2.00	0.03199	1.00	1.00
276	9.13E+10	0.59	1.98	6.53E-04	1.92	0.02585	1.00	0.76
287	8.45E+10	0.61	1.99	6.14E-04	1.90	0.03207	1.00	0.80
297	1.57E+11	0.63	1.99	6.44E-04	1.91	0.03556	1.00	0.82
308	1.53E+11	0.63	1.99	7.41E-04	1.89	0.03776	1.00	0.84
318	1.56E+11	0.63	2.00	8.69E-04	1.89	0.03833	1.00	0.85
328	1.62E+11	0.64	2.00	0.00103	1.89	0.0386	1.00	0.86
332	1.68E+11	0.64	2.00	0.00117	1.89	0.03756	1.00	0.86
342	1.82E+11	0.63	2.00	0.00138	1.87	0.03787	1.00	0.86
352	1.11E+11	0.62	1.99	0.00187	1.89	0.04125	1.00	0.84
362	1.36E+11	0.62	1.96	0.00254	1.92	0.04590	1.00	0.83
372	1.90E+11	0.70	1.93	0.00530	2.00	0.08564	1.00	1.00

Tab. S 11: Number densities for the samples SPAF-303_x with 33 % RH and 67 % RH. It is assumed that n_x is equal to that of the 100% RH samples.^[1]

x	n_x / m^{-3}
0.3	8.58E12
0.5	1.53E13
0.8	7.56E12

- [1] S. F. Winterstein, A. F. Privalov, C. Greve, R. Siegel, B. Pötzschner, M. Bettermann, L. Adolph, J. Timm, R. Marschall, E. A. Rössler, E. M. Herzig, M. Vogel, J. Senker, *J. Am. Chem. Soc.* **2023**, *145*, 27563–27575.

4.3. Thermodynamically Stable Functionalization of Microporous Aromatic Frameworks with Sulfonic Acid Groups by Inserting Methylene Spacers



Article

Thermodynamically Stable Functionalization of Microporous Aromatic Frameworks with Sulfonic Acid Groups by Inserting Methylene Spacers

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Abstract: Porous aromatic frameworks (PAFs) are an auspicious class of materials that allow for the introduction of sulfonic acid groups at the aromatic core units by post-synthetic modification. This makes PAFs promising for proton-exchange materials. However, the limited thermal stability of sulfonic acid groups attached to aromatic cores prevents high-temperature applications. Here, we present a framework based on PAF-303 where the acid groups were added as methylene sulfonic acid side chains in a two-step post-synthetic route (SMPAF-303) via the intermediate chloromethylene PAF (CIMPAF-303). Elemental analysis, NMR spectroscopy, electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy were used to characterize both frameworks and corroborate the successful attachment of the side chains. The resulting framework SMPAF-303 features high thermal stability and an ion-exchange capacity of about 1.7 mequiv g^{−1}. The proton conductivity depends strongly on the adsorbed water level. It reaches from about 10^{−7} S cm^{−1} for 33% RH to about 10^{−1} S cm^{−1} for 100% RH. We attribute the strong change to a locally alternating polarity of the inner surfaces. The latter introduces bottleneck effects for the water molecule and oxonium ion diffusion at lower relative humidities, due to electrolyte clustering. When the pores are completely filled with water, these bottlenecks vanish, leading to an unhindered electrolyte diffusion through the framework, explaining the conductivity rise.

Keywords: covalent organic framework; porous aromatic framework; synthesis; side chain; proton conduction



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1. Introduction

The transport of protons in and through a solid material is a topic that occurs in many applications such as sensors, ion-exchange desalination, CO₂ converters, electrolyzers, and fuel cells [1,2]. The latter devices are receiving more and more attention, due to their broad possible uses [3,4]. In particular, the polymer electrolyte membrane fuel cell (PEMFC) is discussed for application in mobile devices [4–6]. Although PEMFCs are already commercially available, they still need to be further developed [6]. Many types of research focus on the membrane electrode assembly (MEA) [7–9], which constitutes the main part of a PEMFC [10]. It contains the diffusion layers for gas transport, electrodes with the catalyst for the chemical reaction, and the membrane for the proton transport between the two electrodes [11]. In addition to proton transport, there are other requirements placed on the membrane, such as electrical isolation, high thermal stability, and chemical inertness [12].

Despite the research into the MEA, Nafion® and its derivatives are the material of choice [7]. Nafion® is an inert perfluorinated copolymer with a high proton conductivity of up to 0.1 S cm^{−1} at 353 K and 100% RH [13]. Despite its excellent proton conductivity, Nafion® contains disadvantages like high production costs, harmful degradation products,

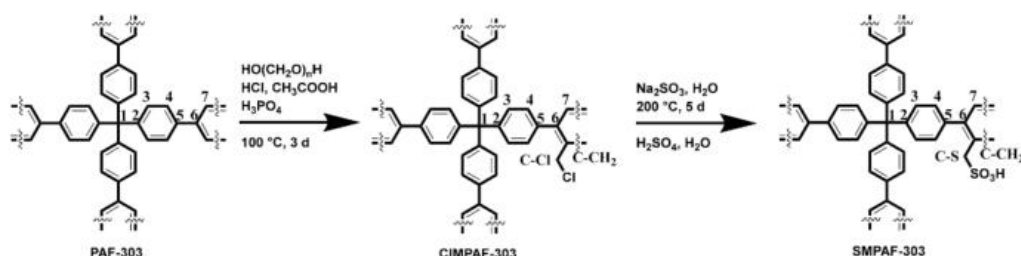
and costly disposal or waste management [14–16]. Moreover, the working temperature of Nafion® is limited to 253 K and 353 K [17,18]. The higher limit is caused by the low retention force that water exhibits in the mesopores of Nafion® [19]. Thus, it is possible to remove the bulk-like water in the inner pore space at higher temperatures quite easily. At the lower temperature limit, water crystallizes, resulting in a strong decrease in the proton conductivity [19,20]. This leads to a complicated water management system for running a PEM-FC with Nafion® to keep a constant hydration level at the operating temperature [21,22].

To increase the confinement and stability of the proton-conducting membrane, several strategies are pursued. Among other things, composite materials consisting of Nafion® are being developed [23–25]. The introduced materials such as metal oxides, acids, metal–organic frameworks (MOFs), and covalent organic frameworks (COFs) increase the uptake of water and the adsorption enthalpy, to increase the operating temperature range. Another focus of research is to find new materials for proton conduction. Porous materials such as carbon materials [8], silica [9], organosilicates [9], MOFs [26,27], and COFs [28,29] with acid groups were developed and investigated according to the ion-exchange capacity and the proton conduction. The introduced sulfonic acid groups led to strong interactions with the adsorbed water molecules [20], high ion-exchange capacities (IECs) and excellent proton conductivities. We already reported sulfonated porous aromatic frameworks (SPAFs), which have an amorphous structure and contain a high ratio of accessible micropores [30,31], whereas the interpenetration of the structure rises with increasing numbers of phenyl rings in the spacers [32,33]. Introducing SO₃H groups to SPAF-2_{0.8}, enabled a six-times higher IEC than Nafion® [31]. Please note that the PAF framework of the SPAF-2 equals the one used for this work but was renamed PAF-303 for consistency with the recent literature [34]. The high charge concentration combined with the adsorbed water phase enables a proton conductivity of about 1 S cm^{−1}. This is supported by water, with a high diffusion coefficient of the water molecules being stored in micropores [31]. Moreover, the sulfonic acid groups are bonded directly to the framework backbone, which leads to a reversible bond, known in organic chemistry as a protection group [35]. This limits the SPAF frameworks in their use in high-temperature applications.

To enhance the thermal and chemical stability of a sulfonic acid proton conductor, the Das group introduced aliphatic C3 and C4 side chains with a terminal sulfonic acid group to UiO-66 [36]. They observed for the C3 side chain the higher conductivity of 1.64 × 10^{−1} S cm^{−1}, caused by the lower pK_A value, due to the shorter chain length. Moreover, these MOFs, especially the CH₂–SO₃H bond, showed excellent thermal and chemical stability. Our aim in this work is to follow this strategy and synthesize a porous aromatic framework that contains sulfonic acid groups that are bound to the framework via an aliphatic side chain. For this, we developed a synthetic strategy that post-synthetically introduces methylenesulfonic acid side chains into PAF-303. The synthesized frameworks were characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, elemental analysis (EA), energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), Ar and water physisorption, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and electrochemical impedance spectroscopy (EIS).

2. Results and Discussion

The synthesis of the methylenesulfonic acid porous aromatic framework (SMPAF-303) was a three-step synthesis starting with the formation of the porous aromatic framework (PAF-303). Second, the methylenechloride group was introduced by a Blanc reaction to the methylenechloride porous aromatic framework (CIMPAF-303) (Scheme 1). Finally, the functional group interconversion (FGI) of the methylenechloride group into the methylenesulfonic acid group leading to the porous aromatic framework (SMPAF-303) was performed.



Scheme 1. Synthesis of sulfonic acid methylene PAF-303 (SMPAF-303) originating from PAF-303 with the intermediate chloromethylene PAF-303 (CIMPAF-303).

The PAF-303 was synthesized according to the protocol of Kaskel et al. [37]. The framework is formed by the 3D-linker tetrakis-(4-bromophenyl)methane and the linear spacer 1,4-phenylenedibronic acid. These two molecules are coupled by a Suzuki cross-coupling reaction with a palladium catalyst. The successful formation of PAF-303 is shown in the IR spectrum (Figure S1, ESI) by the aromatic stretching vibration at 515 cm^{-1} and the para-substituted phenyl out-of-plane bending vibration at 807 cm^{-1} , combined with the absence of the para-substituted ring and stretching vibration of C-Br at 1077 cm^{-1} and the broad stretching vibration of O-H of the boronic acid group at about 3300 cm^{-1} . Moreover, the IR spectrum of PAF-303 does not contain the two overlapping signals of the B-OH vibration and B-Ar out-of-plane deformation vibration, at about $700\text{--}800\text{ cm}^{-1}$. Additionally, the resonances 5 and 6 at 139 ppm in the single-pulse ^{13}C NMR spectrum (Figure 1a) relate to the sp^2 -hybridized carbon demonstrating that the C-C coupling was successful. For the quantification of the cross-coupling degree, the ratio of C-Br (120 ppm) to the C-1 (64 ppm) signal was calculated by deconvolution of the single-pulse (SP) ^{13}C MAS NMR spectra, leading to a cross-coupling degree of 85%, calculated by the 0.6 end groups, for four possible bond formations (Table S1, ESI). Combined with the EA and the EDX measurements (Table S2, ESI), the Suzuki cross-coupling led to a crosslinking degree of 86% and a stoichiometry for PAF-303 listed in Table 1.

Table 1. Stoichiometry of PAF derivatives calculated from Tables S1–S4 (ESI).

Framework	Stoichiometry
PAF-303	$\text{C}_{37}\text{H}_{24}\text{Br}_{0.6}$
CIMPAF-303	$\text{C}_{38}\text{H}_{25}\text{Br}_{0.6}\text{Cl}_{1.2} \times \text{H}_2\text{O}$
SMPAF-303	$\text{C}_{38}\text{H}_{25}\text{Br}_{0.2}\text{SO}_3\text{H} \times 3\text{H}_2\text{O}$

The irreversible bond formation of the Suzuki cross-coupling reaction led to a partial interpenetration for the amorphous framework (Figure S2, ESI), which is already mentioned for PAF-1 by simulation [32,33] and experimentally observed for PAF-303 [31,37]. This interpenetration forms a high number of micropores, which are shown in the strong adsorption of Ar at small partial pressures (<0.05) (Figure 1b). At higher partial pressures the volume increases linearly, with a strong hysteresis over the whole pressure range for desorption. This behavior is typical of a flexible microporous framework like PAF-303. The calculated pore-size distribution from the physisorption measurement gives a broad microporous distribution of pore sizes and a total number of micropores of about 74% (Table 2).

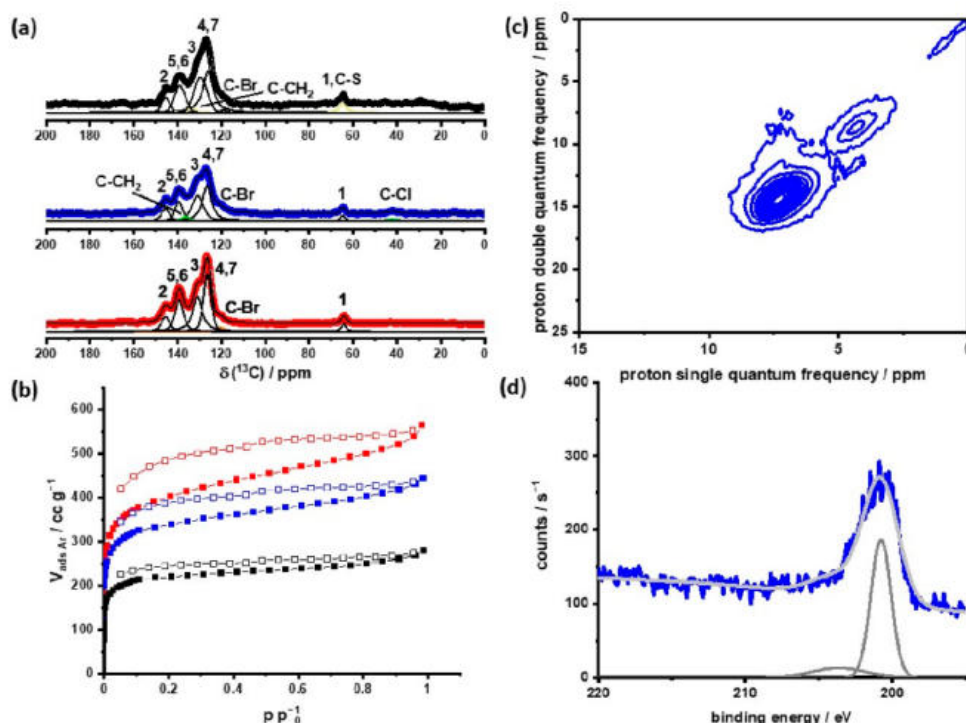


Figure 1. (a) SP ^{13}C MAS NMR spectra of PAF-303 (red), CIMPAF-303 (blue), and SMPAF-303 (black) with corresponding deconvolution and assigned carbon atoms of each structure. (b) Ar physisorption measurements of PAF-303 (red), CIMPAF-303 (blue), and SMPAF-303 (black). The full squares represent the adsorption and the empty ones the desorption. (c) Double quantum ^1H solid-state NMR of CIMPAF-303. (d) Cutout of the XPS spectra of CIMPAF-303 (Figure S3, ESI) showing the Cl 2p signal with the fitting of the two overlapping signals (gray).

Table 2. Ar surface area, total pore volume, and micropore ratio of PAF-303 and its derivatives. * Calculated from the adsorption branch using the BET equation. ** Derived using a QSDFT kernel of the adsorption branch.

Sample	BET SA(Ar)/m ² g ^{−1} *	DFT SA(Ar)/m ² g ^{−1} **	Pore Volume/cc g ^{−1} **	Micropore Ratio/% **
PAF-303	1317	1302	0.681	74
CIMPAF-303	1132	1155	0.539	78
SMPAF-303	743	773	0.337	82

* Calculated using the BET equation. ** Derived using a QSDFT kernel.

This high interconnecting pore space and surface area, where the linker units are well accessible, allows for further reactions [38–41] such as introducing acidic units for proton conduction [30,31]. To achieve the introduction of these chemical- and temperature-stable proton-conducting units in the framework, PAF-303 reacts with formaldehyde and HCl to the intermediate CIMPAF-303 (Scheme 1). The formation of the C-CH₂ bond is corroborated by the two additional signals in the solid-state SP ^{13}C NMR spectrum (Figure 1a) at 41 ppm for the aliphatic side-chain carbon (CH₂-Cl) and 136 ppm for the aromatic carbon to which the side chain is connected. The deconvolution of the SP ^{13}C MAS NMR spectrum (Figure 1a) gives a ratio for the C-1- to CH₂-Cl signal of about one-to-one and for C-1 to the aromatic carbon of about 1.8 (Table S1, ESI). Combined with the results of the EDX

measurements, an average of one side chain per repeating unit of the framework (Table 1) was derived. Moreover, the elemental analysis agrees with the observation from NMR spectroscopy and EDX measurement (Tables S1 and S3, ESI).

The measured DQ-SQ MAS ^1H NMR spectrum (Figure 1c) shows self-correlation signals of the aromatic and aliphatic protons. Additionally, cross-correlation between aromatic and aliphatic protons were observed, confirming that the methylene chloride groups are attached to the aromatic linkers. Furthermore, the X-ray photoelectron spectrum exhibits the carbon and bromine signals that belong to the backbone as end groups (mentioned before), which indicate the stability of the backbone of the framework during the synthesis (Figure S4, ESI). Additionally, a chlorine signal is observed (Figure 1d). The Cl 2p peak splits into two peaks at about 200 and 203 eV. These energies are typically for organic chlorines. Both methods show the successful addition of the formaldehyde to the aromatic unit, and the following conversion to the functional group chloromethylene. In contrast, the IR spectrum (Figure S1, ESI) does not change significantly compared to those of PAF-303, which suggests a small amount of chlorine compared to the number of carbon atoms in the repeating unit.

To introduce sulfonate groups into the framework, the chlorine groups were replaced by SO_3Na . Subsequently, a sodium–proton ion exchange re-established the acid groups. The SP ^{13}C NMR spectrum (Figure 1a, Table S1) shows that the chloromethylene side chains could be transformed quantitatively. Further, it shows an overlapping signal of C-1 at about 65 ppm, which belongs to the quaternary carbon of the 3D linker and the carbon of the $\text{CH}_2\text{-SO}_3\text{H}$ side chain. The quaternary aromatic carbon, where the side chain is connected to the backbone, is at about 130 ppm. Additionally, EDX spectroscopy, EA, and titration (Tables S4 and S5, Figure S4a, ESI) were carried out. On average, one sulfonic acid methylene side group per repeating unit could be introduced, leading to an IEC of 1.73 meq g^{-1} (Table S5, ESI). This IEC is twice as high as the one for Nafion[®] (0.9 meq g^{-1}) [42]. The sulfonation degree x is defined as the number of sulfonic acid groups per benzene rings of the repeating unit. This confirms the stoichiometry of SMPAF-303 with about one sulfonic acid group per repeating unit.

From PAF-303 over CIMPAF-303 to SMPAF-303 the thermal-oxidative stability decreased (Figure S5, ESI). PAF-303's decomposition sets in at about 590 K, which represents the breaking of C-C bonds in the backbone. After chloromethylation, the curve changes in a stepwise decomposition where the first weight loss starts at 480 K, followed by a bigger loss at about 590 K. We assume that the first weight loss is attributed to the side chains, in line with the calculated weight ratio of the side chain to the backbone (one to nine), and that the second one is caused by the decomposition of the framework. SMPAF-303 exhibits a continuous weight loss up to 400 K, which is typical for water loss from a hydrophilic framework (Table 1). The side-chain decomposition sets in at about 500 K, followed by the backbone, as for CIMPAF-303. The first decomposition fits very well with the percentage weight of about 15% of the side chain compared to the whole framework weight. This high-temperature stability compared with the irreversibly bonded sulfonic side chains (Figure S4b and Table S5), which are stable under harsh conditions, offers an ideal basis for use as material for proton conduction in high-temperature fuel cells.

For high-temperature fuel cells, it is necessary to build up a strong confinement. Two parameters influence the confinement strongly. First, the interaction between the sulfonic acid groups and the water molecules, and second the pore size. For the latter, a smaller pore size increases the confinement. Due to the introduction of side chains, the amount of adsorbed gas is reduced, and the corresponding hysteresis becomes smaller (Figure 1b). This trend is also shown in the pore volume, which decreases to about $740 \text{ m}^2 \text{ g}^{-1}$ (DFT surface area $773 \text{ m}^2 \text{ g}^{-1}$) and gives a pore volume of 0.337 cc g^{-1} (Table 2). The introduced side chains reach into the pore, which causes the reduced pore volume (Figure S6). This is already seen in the literature in the post-synthetic modification of PAF by the introduction of other side chains [38,39,43,44].

PAF-303, as well as CIMPAF-303, shows a hydrophobic behavior with a gate opening at 70 and 60% RH (Figure 2a). These trends are caused by the strongly hydrophobic nature of the frameworks compared with the microporosity. The introduction of chloromethylene side chains leads to a decrease in the total water uptake by a factor of roughly two. After substituting chlorine with sulfonic acid groups, the isotherm exhibits a type-II behavior [45]. So, the framework changes its hydrophobic surface into a partially hydrophilic surface, which means a hydrophobic backbone with a hydrophilic side chain that strongly interacts with the adsorbed water molecules. That is shown in the water uptake of SMPAF-303, which increases steadily with higher relative humidity. SMPAF-303 finally reaches the same uptake as PAF-303. This indicates the stronger confinement effect compared to CIMPAF-303 and PAF-303. SMPAF-303 adsorbs the same amount of water with a smaller pore volume than PAF-303 and more water than CIMPAF-303. This strong confinement is shown in DSC measurements (Figure 2b) for samples equilibrated at 33 and 67% RH. At these relative humidities, no freezing and melting of the adsorbed water was observed. For 100% RH, the DSC curves of SMPAF-303 show a melting point with an onset of 256 K (Table S6, ESI). This is typical for 20% of the adsorbed water being stored in inter-particle spaces and mesopores. This is in line with the determined micro- and mesopores calculated from the Ar physisorption measurement and DFT calculations of the pore space (Table 2). Instead, Nafion® contains meso- and macropore water, which leads to the freezing of about 40% of water at about 263 K [19,46]. This large amount of non-freezable water results in a limitation of the working temperature, which is already known in the literature [17,18].

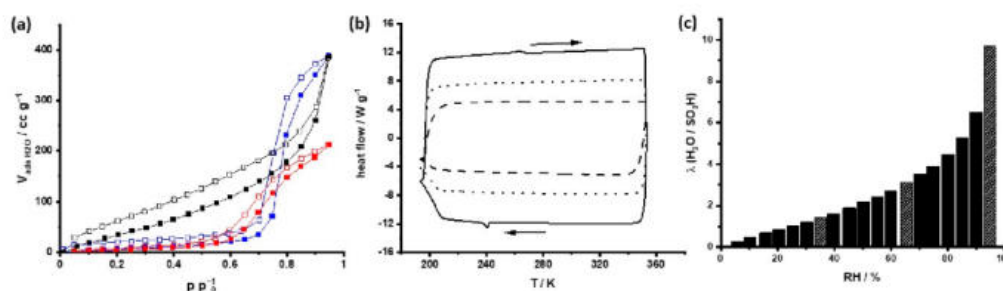


Figure 2. (a) H₂O physisorption measurement of PAF-303 (blue), CIMPAF-303 (red), and SMPAF-303 (black) at 298 K. The full squares represent the adsorption and the empty ones the desorption. (b) DSC measurements of SMPAF-303 at 33 (dashed), 67 (dotted), and 100 (lined) % RH. (c) λ , calculated from H₂O physisorption measurement, against relative humidity. The relative humidities of 33, 67, and 98% are highlighted by hatching.

SMPAF-303 is able to store about 31 wt.-% of water. A total of 80% of the water is absorbed in micropores. The limited uptake of water due to the uptake of PAF-303 is caused by the fact that the framework contains, next to the hydrophilic side chains, the hydrophobic backbone, which limits the total water uptake. The number of water molecules per sulfonic acid group (λ) is a value for the comparison of proton-conducting materials. SMPAF-303 has up to about 10 H₂O/SO₃[−] for 100% RH. With decreasing RH, λ is also reduced, with an exponential trend (Figure 2c). The state-of-the-art material Nafion® [46] has about 14 water molecules per sulfonic acid group. This means that the charges of the hydroxonium ions are influencing each other much more in SMPAF-303 than in Nafion®.

The high charge-carrier concentration (1.83 meq g^{−1}) at a relatively low λ , the strongly adsorbed water molecules up to 31 wt.-%, and the irreversible bonded sulfonic acid groups make SMPAF-303 a promising proton-conduction material. To determine the proton conduction at a temperature range from room temperature to 353 K, the powder was saturated under 33, 67, and 100% RH and pressed to a pellet. The EIS spectra were simulated with an equivalent circuit containing one preliminary resistance (R_E) and three RC elements in series (Figure S7, ESI). This type of equivalent circuit is typically used

for water-mediated microporous proton conductors, which are placed in a parallel-plate capacitor-like setup [31,47]. In the used equivalent circuit, the R_E simulates the connection of the cables to the measurement setup. This element is negligible at larger impedances, such as for the measurements for 33% RH and 67% RH. For all relative humidities, the first two semicircles belong to bulk and grain boundaries, and the third one to the electrode interface (Figure 3 and Figure S8–S10, ESI).

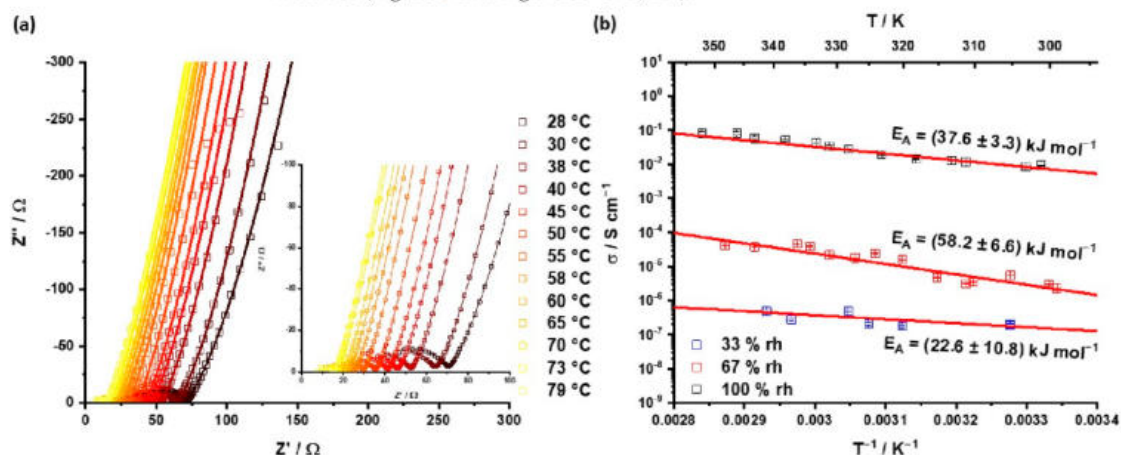


Figure 3. (a) Nyquist plot of SMPAF-303 at 100% RH with an enlarged image section of the semi-circle of the bulk proton conductivity. (b) Arrhenius plot of the conductivity of SMPAF-303 EIS measurements at 33 (empty), 67 (half-filled), and 100 (full) % RH with a linear fit and the calculated activation energy.

Saturating at 33% RH leads to a high protonation level of water, where two-thirds of the water molecules are protonated and λ is 1.4, which leads to strong ion interactions between the oxonium ions and the SO_3^- groups, leading to strong ion-pair interactions. Additionally, the movement of protons is limited in the bulk and in the grain boundaries, which results in the same order of capacities for both RC elements (Table S7, ESI). For λ equal to 3, which is realised when saturating at a relative humidity of 67% RH, the separation between the bulk- and grain-boundary semicircles becomes visible. This higher water content results in an unsaturated solvation shell of the oxonium ions and separates the charges from each other. At 100% RH there is a clear separation between the bulk- and grain-boundary conductivities, as well as of the electrode (Figure 3a). Here, λ is about 10, which enables a free water diffusion. This leads to a better solvation of oxonium ions, resulting in higher shielding of the opposite charges to each other than for 67% RH. This stronger separation increases the mobility of the charged carriers shown by lower resistances (Table S8, ESI). The low resistances induce the conduction resistance of the electrode to be visible as electrode resistance (Figure 3a).

The conductivities of the three relative humidities are calculated from the bulk resistances. SMPAF-303 reaches conductivities from 10^{-7} to $10^{-1} S\ cm^{-1}$ (Figure 3b). For 33% and 67% RH, bulk- and grain-boundary conductivities are on the same order of magnitude (Tables S7 and S8, ESI). This behavior is untypical, and can be explained by an unsaturated solvation shell of the oxonium ions in the pores and strong ion interactions, which lead to an immobilization of the charges. Additionally, we suggest alternating hydrophilic and hydrophobic areas. The hydrophilic regions are close to the side chains, and the hydrophobic regions are the aromatic backbone without side chains.

In contrast, at 100% RH, bulk- and grain-boundary conductivities increase strongly (Table S9, ESI). We attribute this to the higher λ (Figure 2c) rather than to lower humidities. About 10 H_2O molecules per sulfonic acid group lead to a sufficient hydration shell of the oxonium ion and, concomitant with the separation of this ion, to their counterion.

This results in a high conductivity of 0.1 S cm^{-1} at 350 K and lower activation energy, compared to lower humidities of about 38 kJ mol^{-1} (Figure 3b). This high conductivity, which is in the same order as Nafion® [13], suggests a free diffusion of water molecules and oxonium ions through the framework, which is typical for microporous materials [31]. Compared to SPAF-2, SMPAF-303 is one decade lower [31]. This difference results in an alternating polarity in the framework structure, which hinders the free diffusion in SMPAF-303, compared to SPAF-2. We suggest that the conductivity can be increased with a higher side-chain concentration to form a constant diffusion pathway through the framework.

3. Material and Methods

3.1. Materials

All chemicals and solvents which are used for the synthesis were commercially available and were of reagent grade, without further purification. 1,1'-Bis(di-isopropylphosphino)ferrocene (DIPPE, 98%) was purchased from abcr. 1,4-Phenylenediboronic acid (BDB, >97%) and tetrakis(triphenylphosphino)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$, >97%) were purchased from TCI. Glacial acid (conc.), sodium sulfite (>95%), and sulfonic acid (95–97%) were purchased from Merck KGaA. Ethanol (99.3%) was purchased from VWR-Chemicals. Potassium carbonate (>99%), paraformaldehyde (95%), and zinc (II) chloride (98%) were purchased from Sigma-Aldrich. Tetrahydrofuran (>99.5%) was purchased from Berndt-Kraft. Hydrochloric acid (37 wt.-%) was purchased from Grüssig. The cross-coupling reaction was carried out under Ar atmosphere. Ar (purity 5.0) was passed through zeolite, P_2O_5 , and the BTS catalyst column.

The equilibration of SMPAF-303 was carried out under an atmosphere with controlled relative humidity. The equilibration was carried out for 48 h at 33, 67, and 100% RH, using a saturated salt solution or water.

3.2. PAF-303

For the tetrakis-(4-bromophenyl)methane (Br-TPM), 477 mg (0.75 mmol, 1 eq.) was put into a flask with 251 mg (1.5 mmol, 2 eq.) 1,4-phenylenediboronic acid and 13.6 mg (32.5 μmol , 0.04 eq.) 1,1'-bis(diisopropylphosphino)ferrocene. A total of 37.6 mg (32.5 μmol , 0.04 eq.) tetrakis-(triphenylphosphino)palladium(0) was added, with 15 mL degassed 2 M K_2CO_3 solution and 130 mL THF under an inert gas atmosphere. The solution was boiled under reflux at 393 K for 24 h. When the reaction was complete the solid was filtered off, and washed with THF, EtOH, H_2O , and 2 M HCl, three times. The beige solid was purified with EtOH Soxhlett and additionally dried under reduced pressure. Yield: 198 mg (0.42 mmol, 56%).

3.3. CIMPAF-303

Paraformaldehyde (503 mg, 16.7 mmol) was dissolved in 10 mL conc. HCl. Additionally, 1.5 mL conc. phosphoric acid, 3 mL acetic acid, 124 mg (0.9 mmol) ZnCl_2 , and 101 mg (215 μmol) PAF-303 were immediately added, and the high-pressure flask was sealed. The suspension was heated up to 383 K for five days, filtered off, purified by Soxhlett (1:1, EtOH: H_2O), and dried under reduced pressure. Yield: 103 mg (200 μmol , 93%).

3.4. SMPAF-303

To synthesize SMPAF-303, 60 mg (105 μmol) of CIMPAF-303 was added to 20 mg (161 mmol) Na_2SO_3 and 12.15 mL water in a hydrothermal high-pressure vessel and heated up to 473 K, for five days. The resulting framework was protonated by 1 M H_2SO_4 and washed with water. Yield: 43.5 mg (77 μmol , 73%).

3.5. Methods

IR measurements were carried out on a JASCO FT/IR-6100 Fourier-transform IR spectrometer with an attenuated total reflectance unit. Ar physisorption measurements were carried out on an Autosorb I at 87 K with Ar as adsorbate. Water physisorption

measurements were carried out at 293 K on an Autosorb IQ-MP-MP-AG setup (Anton Paar, QuantaTec, Boynton Beach, FL, USA). All samples were degassed for 12 h at 393 K under reduced pressure. The measurements were analyzed with the software package ASiQ ver. 3.0. CHNS analysis was carried out on an ELEMENTAR UNICUBE with sulfanilamide as a reference. Powder X-ray diffraction measurements were carried out on a STOE STADIP diffractometer with a Ge(111) monochromator and Cu-K α radiation. For the measurement, the frameworks were placed in 1.0 mm capillaries and measured at KI in Debye–Scherrer geometry. Thermogravimetric analysis (TGA) was measured on a Mettler Toledo TGA/SDTA851e under air atmosphere in the temperature range from 303 to 973 K with a heating rate of 10 K min^{-1} . The differential scanning calorimetry (DSC) measurements were carried out on a Mettler Toledo DSC/SDTA 821e DSC with an autosampler in the temperature range from 193 to 353 K with 5 K min^{-1} under a nitrogen atmosphere with three heating cycles. For the evaluation, the third cycle was used. The samples were equally saturated at 33, 67, and 100%, as described above. The p*H* values for the titration curves were measured with a Mettler Toledo seven2go pH meter. The titration was carried out with an aqueous 0.8163 mM NaOH solution.

X-ray photoelectron spectroscopy (XPS) measurements were made with a PHI 5000 VersaProbe III system fitted with an Al K α excitation source ($h\nu = 1486.6\text{ eV}$) and a dual neutralizer (electron and Ar⁺ gun) at 10–10 mbar. The source diameter of the X-ray beam was 100 μm . The multichannel analyzer collected the corresponding photoemission with 45° take-off angle. The pass energies of 292.5 and 69 eV were used for the measured spectra. The analysis of the spectra was carried out with a Multipak software pack version 9.9 provided by the manufacturers. The ^{13}C single-pulse solid-state NMR spectra were measured on a Bruker Avance III HD spectrometer with a B0 field of 9.4 T. The pulse length was 3.20 μs , and the recycle delay was set to 120 s. The ^1H – ^1H double-quantum (DQ) single-quantum (SQ) spectra were recorded on a Bruker Avance III spectrometer operating at a magnetic field strength of 14.1 T, using an R18 π^5 ($\nu(^1\text{H}) \approx 62.5\text{ kHz}$) recoupling sequence with an S $_0$ S $_{\pi}$ supercycle. The DQ excitation time was set to multiples of one RR' block (22.22 μs): 111.11, 155.56, 2000.00, and 244.44 μs , and a recycle delay of 2.0 s was chosen.

Impedance measurements were made on a Novocontrol Alpha Analyzer with ZG4 and a 5 mV AC voltage was applied. The frequency range was set to 4 MHz to 1 Hz. The samples were placed between two steel electrodes to build a capacitor-like setup. SMPAF-303 was equilibrated under controlled relative-humidity gas flow for one day. The sample was conducted with the metal electrodes and the pressure was set to about 200 bar. The relative humidity of the atmosphere was constant during the measured temperature range. The equilibration time for every temperature step was 30 min. After the measurement, the length *l* and conduction area *A* were determined. The conductivity was calculated according to the formula $\sigma = l(\pi r^2 R)^{-1}$, $r = 4\text{ mm}$. *R* is the resistance from the high-frequency semicircle of the Nyquist plot (Cole plot). The resistance was simulated with the equivalent circuit (Figure S7, ESI) in RelaxIS 3.

4. Conclusions

In this work, we report on the synthesis of an innovative new material for proton conduction. The synthesis route follows two post-synthetic modifications. The first step is the addition of a CH $_2$ –Cl side-chain unit via Blanc reaction to CIMPAF-303. The second one is the substitution of the chlorine by a sulfonic acid group by functional group interconversion to SMPAF-303. Introducing the CH $_2$ –SO $_3\text{H}$ side chains into the microporous framework increases its ability to adsorb water. For 100% RH, the moderate grafting density of one side chain per repeating unit led to λ of 10 H $_2\text{O}/\text{SO}_3^-$. Water adsorption and proton conductivities measured as a function of the water uptake suggest that the framework shows an alternation in polarity. The strong interactions between water molecules and the sulfonic acid group increase the polarity, whereas the aromatic backbone limits the affinity for water. This restricts the free diffusion of oxonium ions through the pores, particularly for low RH. Only at high relative humidities are the pores completely filled, which ensures free diffusion

of the oxonium ions and high conductivity, as for Nafion[®]. Due to the irreversibly bonded SO₃H groups, SMPAF-303 is a promising framework for proton-conducting materials, which warrants further studies to increase its IEC and conductivity.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules29071666/s1>, Figure S1: IR spectra of BDB, BrTPM, PAF-303, CIMPAF-303, and SMPAF-303; Table S1: Ratio of the NMR integrals from deconvolution (Figure 1a); Table S2: Composition of PAF-303; Figure S2: Powder XRD diffractogram of PAF-303, CIMPAF-303, and SMPAF-303; Table S3: Composition of CIMPAF-303; Table S4: Composition of SMPAF-303; Figure S3: XPS spectrum of CIMPAF-303; Figure S4: Titration curves of SMPAF-303; Table S5: Experimental data of the titration curves; Figure S5: TGA measurements of PAF-303, CIMPAF-303, and SMPAF-303; Table S6: Experimental data of DSC curves; Figure S6: Pore-size distribution and cumulative pore volume of PAF-303, CIMPAF-303, and SMPAF-303; Figure S7: Equivalent circuit for impedance measurements; Figure S8: Nyquist plot of impedance measurement of SMPAF-303 at 33% RH; Table S7: Fitting data of impedance measurement of SMPAF-303 at 33% RH; Figure S9: Nyquist plot of impedance measurement of SMPAF-303 at 67% RH; Table S8: Fitting data of impedance measurement of SMPAF-303 at 67% RH; Figure S10: Nyquist plot of impedance measurement of SMPAF-303 at 100% RH; Table S9: Fitting data of impedance measurement of SMPAF-303 at 100% RH.

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Supporting Information

Thermodynamically Stable Functionalization of Microporous Aromatic Frameworks with Sulfonic Acid Groups by Inserting Methylene Spacers

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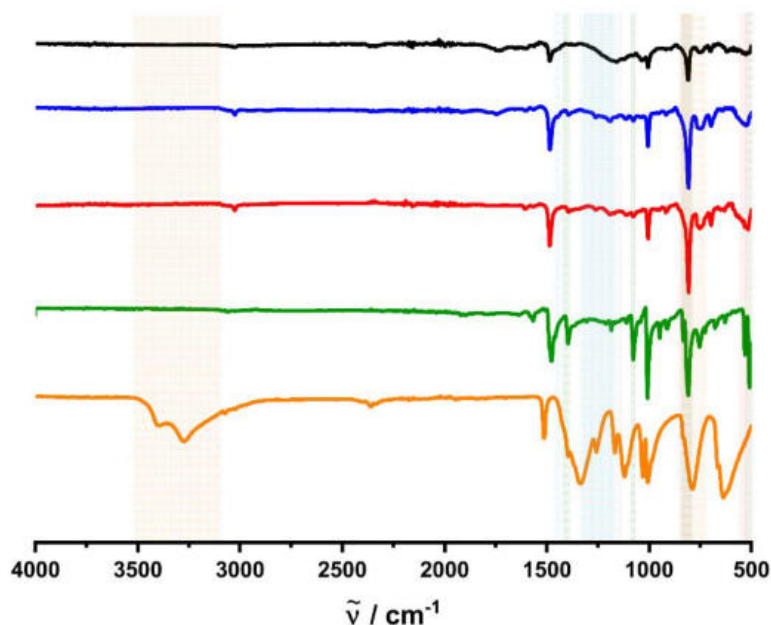


Figure S1: IR spectra of BDB (orange), BrTPM (green), PAF-303 (red), CIMPAF-303 (blue), and SMPAF-303 (black) with characteristic bands in the corresponding color.

Table S1: Ratio of the NMR integrals from deconvolution (Figure 1a). The ratio is normalized to the carbon atoms of the structure. The stoichiometry calculated by NMR is equal to the integrals because the C-1 integral represents the repeating unit with 37 or 38 C atoms.

framework		C	Br	Cl	S
PAF-303	Integral C-1 to C-Br	1	0.60		
	Normalized to 37 C atoms at.-%	37	0.6		
CIMPAF-303	Integral C-1 to C-Br, CH ₂ -Cl ^a and C-CH ₂ ^b	1	0.67	1.09 ^a /1.79 ^b	
	Normalized to 38 C atoms at.-%	38	0.7	1.1 ^a /1.8 ^b	
SMPAF-303	Integral C-1 to C-Br, CH ₂ -S ^a and C-CH ₂ ^b	1	0.34		1 ^c /0.91 ^b
	Normalized to 38 C atoms at.-%	38	0.3		1 ^c /0.9

^a Integral of C-Cl, which is overlapping with the quaternary carbon C-1

^b Integral of the aromatic carbon at which the side chain is connected to

^c Integral of C-S, which is overlapping with the quaternary carbon C-1

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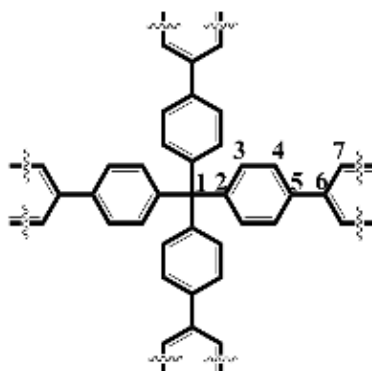


Table S2: Composition which was calculated from EA, EDX, and NMR of PAF-303. The composition was normalized to 37 C atoms that correspond to the repeating unit of PAF-303. The bromine value normalized to 37 C determined from NMR is the same as the integral from C-Br normalized to the integral of C-1. C-1 represents one repeating unit with 37 C.

PAF-303		C	H	N	S	Br
Composition	at.-%	37	24	--	--	0.6
EA	wt.-%	82.95	4.56	0.12	0.15	--
	at.-%	6.91	4.53	0.01	0.00	--
	Normalized to 37 C atoms at.-%	37	24.26	0.05	0.03	--
EDX	at.-%	91.78				1.26
	Normalized to 37 C atoms at.-%	37				0.5

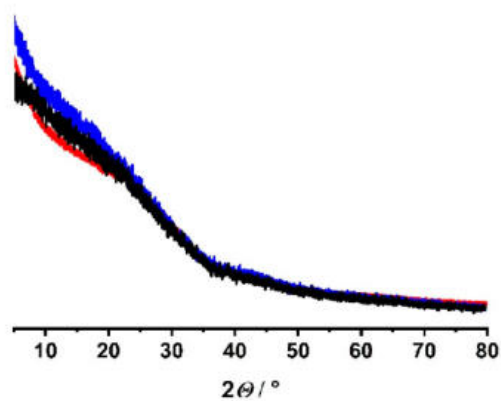


Figure S2: Powder X-ray diffractogram of PAF-303 (red), ClMPAF-303 (blue), and SMPAF-303 (black).

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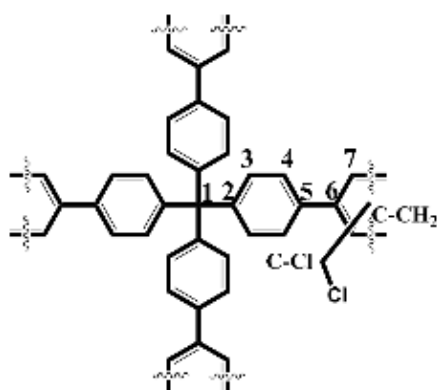


Table S3: Composition which was calculated from EA, EDX, and NMR for CIMPAT-303. The composition was normalized to 38 C atoms that correspond to the repeating unit of CIMPAT-303.

CIMPAT-303		C	H	N	S	Br	Cl
Composition	at.-%	38	26.9	--	--	0.6	1.2
EA	wt.-%	80.38	4.78	0.12	0.37	--	
	at.-%	6.69	4.74	0.02	0.15	--	
	Normalized to 38 C atoms at.-%	38	26.9	0.1	0.1	--	
EDX	at.-%	90.07				1.25	1.43
	Normalized to 38 C atoms at.-%	38				0.5	0.6

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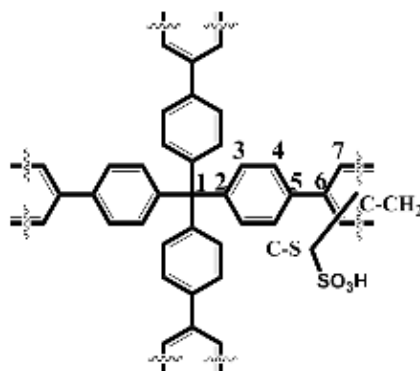


Table S4: Composition which was calculated from EA, EDX, and titration. The composition was normalized to 38 C atoms that correspond to the repeating unit of SMPAF-303.

SMPAF-303		C	H	N	S	Br	Cl
Composition	at.-%	38	31.9	–	1	0.2	–
EA	wt.-%	67.92	4.78	0.35	4.96	–	–
	at.-%	5.65	4.74	0.02	0.15	–	–
	Normalized to 38 C atoms at.-%	38	31.9	0.2	1.0	–	–
EDX	at.-%	79.3	–	–	2.3	0.3	–
	Normalized to 38 C atoms at.-%	38	–	–	1.1	0.1	–
Titration	Normalized to 38 atoms at.-%	38	–	–	1.0	–	–

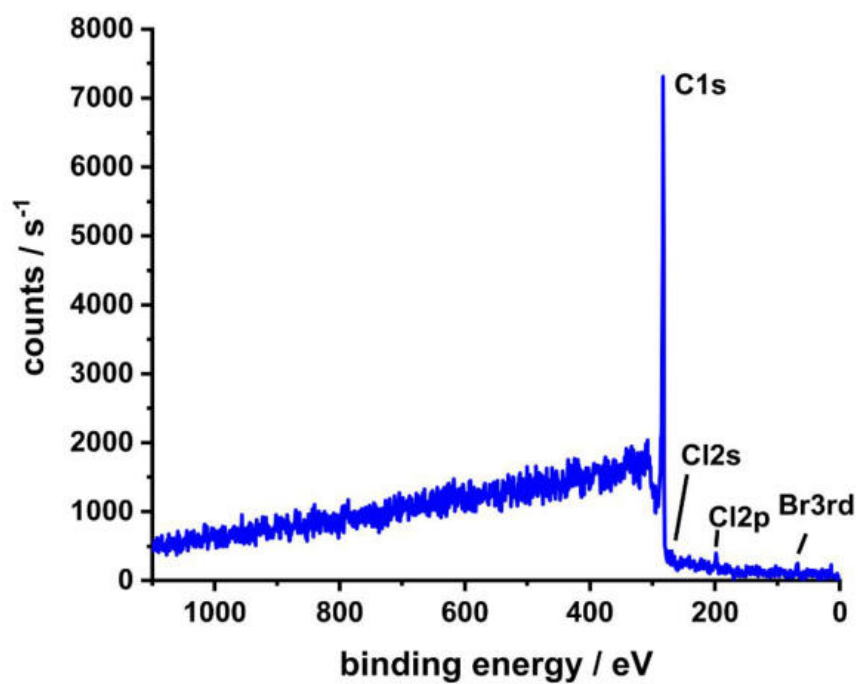


Figure S3: XPS spectrum of CIMPAPF-303 after sputtering the sample with Ar.

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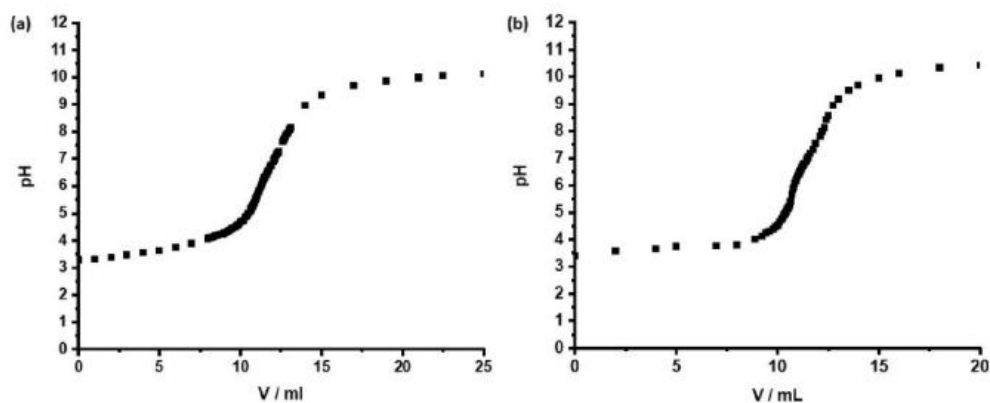


Figure S4: Titration curve of SMPAF-303 with 0.8163 mM NaOH solution after synthesis (a) and after characterization and stability test of the framework (b) To test the irreversible bond formation of C-S, the framework was stirred in 1 M HCl at 253 K for 24 h. The framework was filtered off, washed with water and the SO_3H groups were determined.

Table S5: Experimental data according to Figure S5, sulfonation degree x and ion exchange capacity (ICE) calculated from titration.

sample	weight / mg	V_{EP} / ml	X / %	ICE
SMPAF-303 after synthesis	5.5	11.63	100	1.73
SMPAF-303 after experiments	5.4	11.47	100	1.73

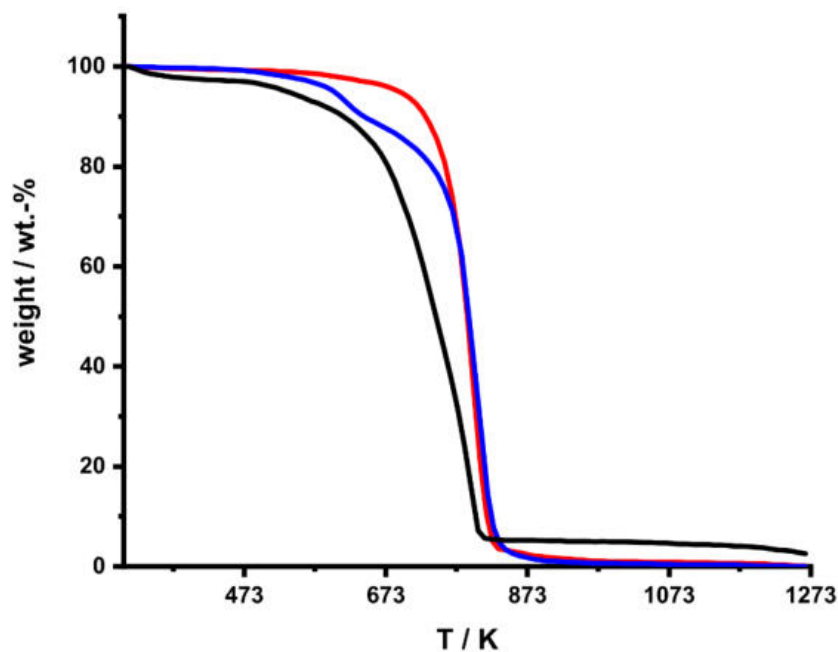


Figure S5: TGA measurements of PAF-303 (red), CIMPAF-303 (blue), and SMPAF-303 (black).

Table S6: Onset of melting point and melting enthalpy of SMAPF-2 from DSC curve (figure 2b).

framework	33 %-rh		67 % rh		100 %	
	T_m / K	$\Delta_m H$ / J	T_m / K	$\Delta_m H$ / J	T_m / K	$\Delta_m H$ / mJ
SMPAF-303	--	--	--	--	256	26.9

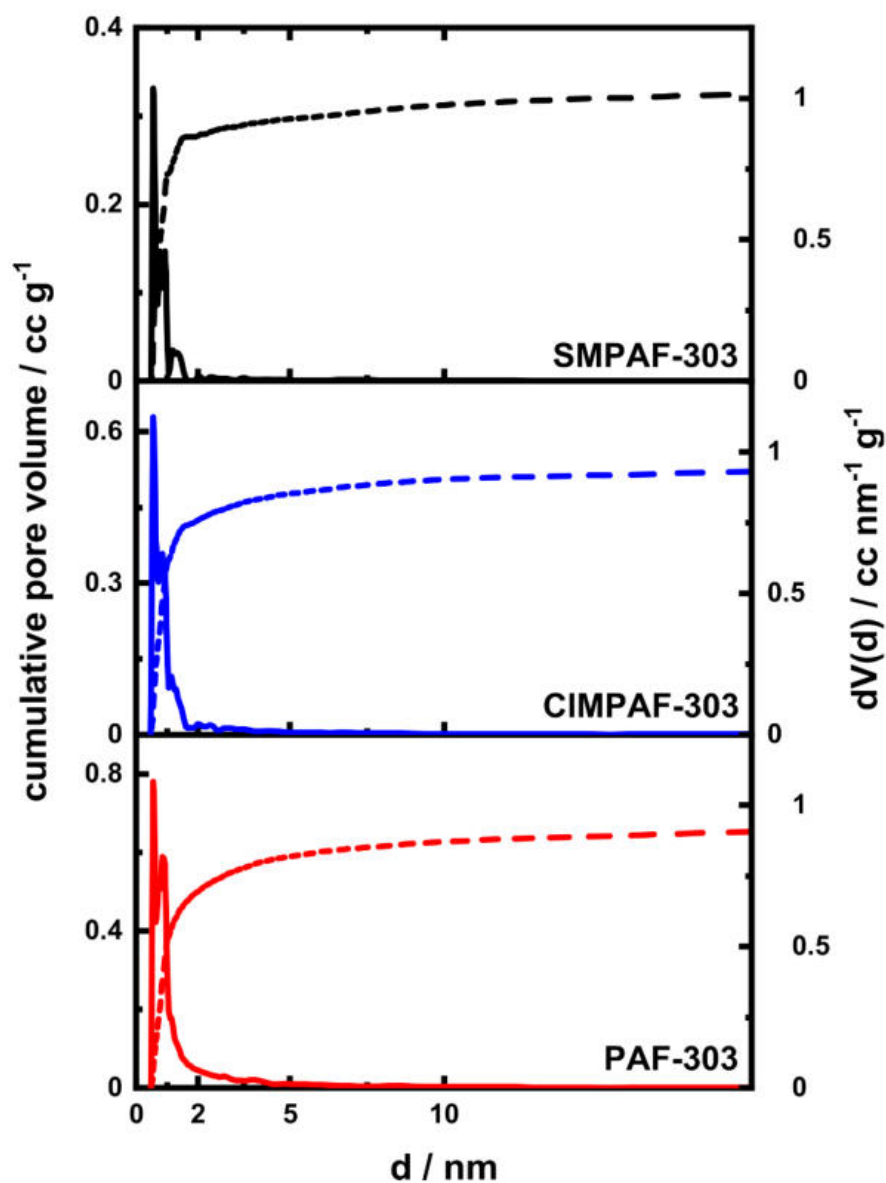


Figure S6: Pore size distribution (lined) and cumulative pore volume (segmented) calculated with DFT simulation (kernel: Ar at 87 K on carbon QSDFT (slit pore, QSDFT equilibrium model)) where the adsorption branches were used from the Ar isotherms of Figure 1b.



Figure S7: General equivalent circuit for impedance measurements of SMPAF-303, containing a preliminary resistance (R_E) for the electrical conductivity and three in-series connected resistances (R) - constant-phase-elements (CPE).

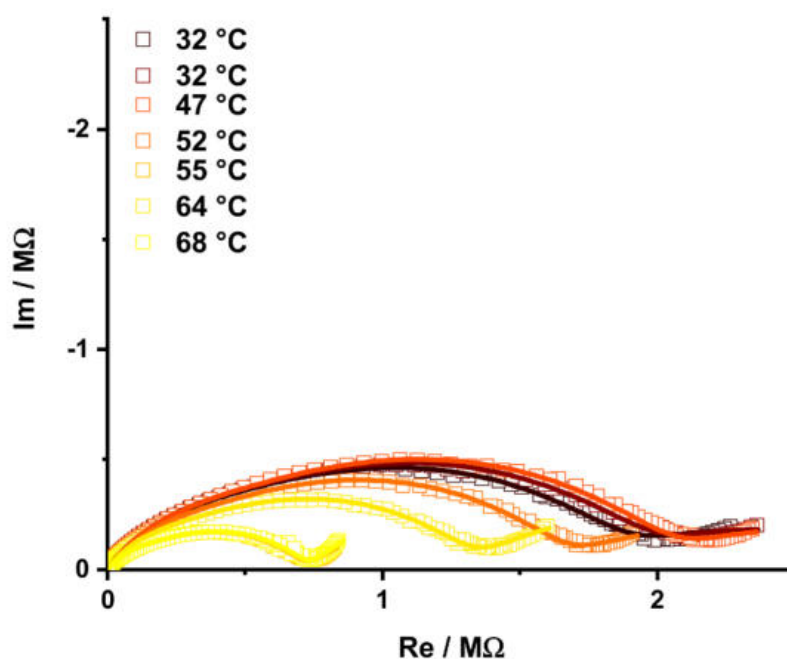


Figure S8: Nyquist plot of SMPAF-303 at 33 % RH with an enlarged image section of the proton conductivity.

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Table S7: Simulation parameters of SMPAF-303@33 % RH.

T / K	bulk			grain boundaries			electrode interface		
	$R_B / k\Omega$	$CPE_B / 10^{-9} S$	α_B	$R_{GB} / M\Omega$	$CPE_{GB} / 10^{-9} S$	α_{GB}	$R_{EI} / k\Omega$	$CPE_{EI} / 10^{-6} S$	α_{EI}
305	363 (90)	1.56 (27)	0.74 (3)	1.50 (15)	6.60 (43)	0.64(3)	856(278)	1.55(20)	0.47(11)
305	390 (96)	1.58 (27)	0.74 (3)	1.57 (16)	6.58 (43)	0.64(3)	877(302)	1.55(20)	0.47(12)
320	350 (83)	1.57 (30)	0.74 (3)	1.69 (14)	6.51 (39)	0.63(2)	891(516)	2.26(28)	0.46(16)
325	265 (62)	1.61 (33)	0.75 (3)	1.39 (11)	6.92 (41)	0.63(2)	943(658)	2.87(27)	0.45(15)
328	104 (18)	1.83 (42)	0.76 (3)	0.60(2)	9.98 (31)	0.62(1)	1E12(--)	7.46(30)	0.41(2)
337	219 (46)	1.73 (33)	0.74 (3)	1.09(7)	7.77 (41)	0.63(2)	138(878)	2.79(16)	0.45(10)
341	116 (32)	2.10 (69)	0.74 (4)	0.61(4)	10.4 (5)	0.62(2)	1E12(--)	6.68(33)	0.48(3)

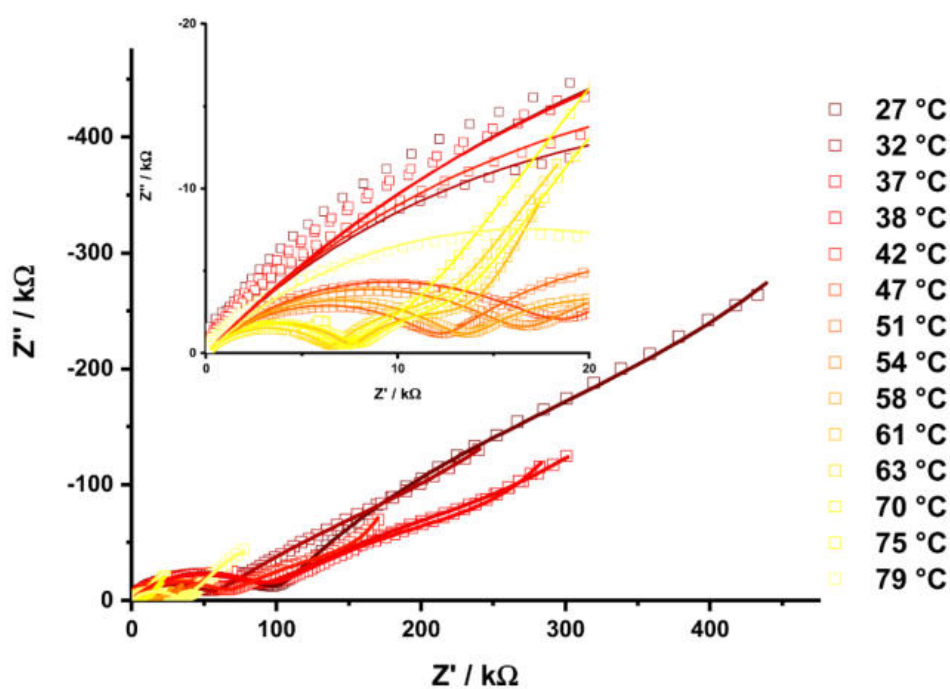


Figure S9: Nyquist plot of SMPAF-303 at 67 % RH with an enlarged image section of the proton conductivity.

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Table S8: Simulation parameters of SMPAF-303@67 % R11.

$T /$ K	bulk			grain boundaries			electrode interface		
	$Z_b / k\Omega$	$CPE_b / 10^{-8} S$	α_b	$R_{GB} / k\Omega$	$CPE_{GB} / 10^{-5} S$	α_{GB}	$R_{ei} / 10^{11} \Omega$	$CPE_{ei} / 10^{-5} S$	α_{ei}
299	133(2)	1.63(8)	0.56(0)	58.7(8.0)	0.44(2)	0.76(3)	5.51	1.00(8)	0.34(2)
300	101(1)	1.86(14)	0.55(1)	357(53)	0.19(1)	0.62(1)	1E4	0.67(10)	0.72(6)
305	54.7(1.1)	2.76(35)	0.57(1)	235(100)	0.41(5)	0.48(2)	1E4	1.37(59)	0.66(13)
310	85.9(1.4)	2.32(17)	0.57(1)	367(85)	0.27(2)	0.46(2)	3.01E-6	2.77(1.23)	1.00(19)
311	94.5(1.1)	2.58(17)	0.56(1)	253(22)	0.25(1)	0.50(1)	9.58E3	2.05(23)	0.89(5)
315	63.6(1.1)	2.69(27)	0.57(1)	162(22)	0.44(3)	0.47(2)	1E4	3.73(5.52)	1.00(8)
320	18.8(1)	6.63(38)	0.54(0)	34.9(2.7)	0.92(3)	0.56(1)	1.70E-6	7.02(59)	0.83(7)
324	12.4(1)	6.90(36)	0.55(0)	19.2(6)	1.25(4)	0.58(1)	3.08E-7	11.9(5)	0.99(3)
327	16.8(1)	6.61(23)	0.54(0)	14.1(3)	1.07(3)	0.59(1)	1E4	10.9(2)	0.75(1)
331	13.7(1)	6.38(25)	0.55(0)	9.99(25)	1.26(4)	0.60(1)	1E4	12.9(2)	0.77(1)
334	7.70(5)	7.52(60)	0.56(1)	6.33(24)	1.66(10)	0.65(2)	1E4	14.9(3)	0.75(1)
336	6.58(5)	8.98(83)	0.55(1)	6.55(59)	2.18(15)	0.63(2)	1.21E-6	11.1(3)	0.76(4)
343	7.94(6)	7.88(64)	0.55(1)	6.20(58)	2.30(20)	0.59(2)	1.18E-6	8.35(19)	0.77(3)
348	7.28(7)	6.78(70)	0.57(1)	4.01(82)	3.56(56)	0.57(4)	2.62E-6	5.73(12)	0.71(3)

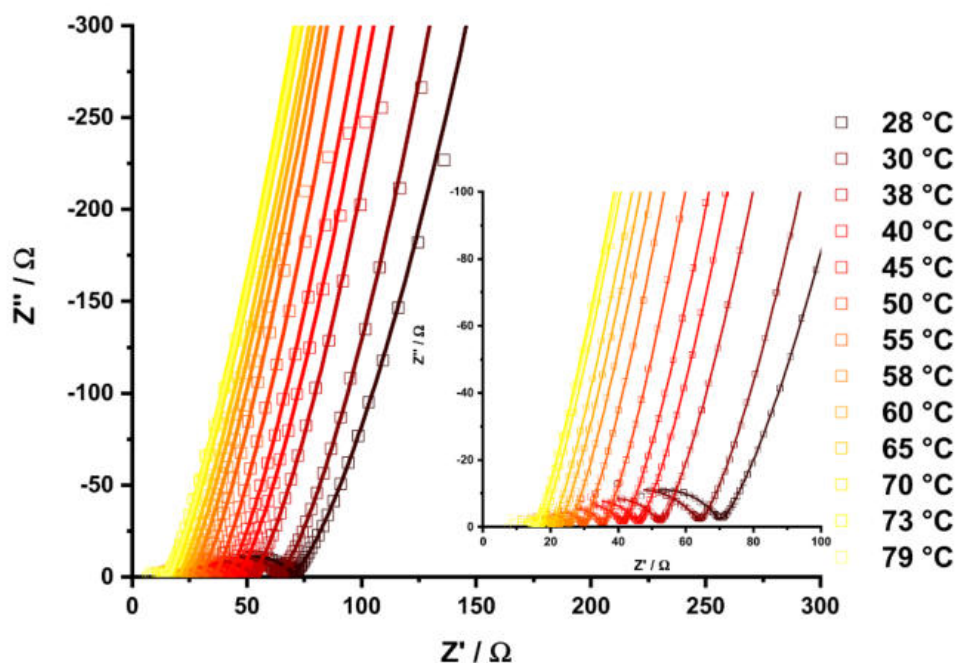


Figure S10: Nyquist plot of SMPAF-303 at 100 % RH with an enlarged image section of the proton conductivity.

Table S9: Simulation parameters of SMPAF-303@100 % RH.

T / K	elec- trode	bulk			grain boundaries			electrode interface		
	R_E / Ω	R_B / Ω	$CPE_B / 10^{-8} S$	α_B	$R_{GB} / \Omega *$	$CPE_{GB} / 10^{-3} S$	α_{GB}	$R_{EI} / \Omega *$	$CPE_{EI} / 10^{-5} S$	α_{EI}
301	38.7(7)	30.4(9)	3.04(56)	0.79(1)	80.6	1.29(28)	0.44(2)	1E15	1.56(30)	0.89(5)
303	30.1(7)	33.4(8)	5.41(65)	0.73(1)	54.0	0.94(12)	0.49(1)	7E14	1.16(9)	0.91(2)
311	27.9(6)	23.9(7)	4.66(66)	0.77(1)	77.3	1.23(58)	0.47(3)	1E15	1.17(21)	0.91(5)
313	23.7(5)	21.7(6)	4.62(64)	0.77(1)	46.1	1.48(22)	0.47(1)	2E13	1.24(10)	0.91(2)
318	21.6(5)	19.3(5)	5.07(67)	0.77(1)	42.0	1.52(22)	0.47(1)	1E13	1.27(9)	0.91(2)
323	20.1(6)	14.6(7)	3.29(80)	0.81(2)	70.6	2.35(332)	0.44(10)	4E12	1.34(54)	0.91(13)
328	18.6(5)	10.3(6)	2.06(70)	0.87(3)	90.1	3.91(458)	0.41(9)	1E13	1.53(12 1)	0.90(37)
331	16.3(4)	8.49(51)	1.92(72)	0.88(3)	963	5.49(282)	0.39(5)	3E12	1.84(7)	0.89(1)
333	15.2(3)	6.50(45)	9.15(44)	0.95(3)	4E6	0.02(1)	0.88(1)	3E12	988(608)	0.34(6)

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338	14.0(3)	5.57(43)	1.12(61)	0.95(4)	2F3	9.76(686)	0.35(7)	8E14	2.08(9)	0.88(1)
343	12.0(3)	4.91(52)	2.48 (151)	0.91(4)	6.81	3.10(293)	0.48(9)	1E15	2.22(15)	0.87(1)
346	11.8(3)	3.49(41)	1.16 (127)	1.00(7)	5E3	0.17(6)	0.93(9)	1E15	102(250)	0.55(18)
352	12.2(2)	3.46(38)	1.12 (108)	1.00(6)	5E3	0.17(99)	0.93(36)	266	109(247)	0.54(18)

*No fitting error is reported because of the fitting error larger than 100 %.

5. Publikationsverzeichnis

- I) C. Klumpen, S. Winterstein, G. Papastavrou, J. Senker, *J. Mater. Chem. A* **2018**, *6*, 21542-21549.

- II) S. Schönfeld, F. Baier, J. Jungklaus, G. Hörner, S. Winterstein, A. Enders, J. Senker, B. Weber, *J. Appl. Phys.* **2021**, *129*, 083901.

- III) S. F. Winterstein, A. F. Privalov, C. Greve, R. Siegel, B. Pötzschner, M. Bettermann, L. Adolph, J. Timm, R. Marschall, E. A. Rössler, E. M. Herzig, M. Vogel, J. Senker, *J. Am. Chem. Soc.* **2023**, *145*, 27563-27575.

- IV) S. F. Winterstein, M. Bettermann, J. Timm, R. Marschall, J. Senker, *Molecules* **2024**, *29*, 1666.

- V) Understanding of Proton Conduction in Confinement of SPAF-303 (Manuskript, **2025**)

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